THE DETERMINATION OF SEVERAL METALS IN ORGANIC SEPARATES OF SELECTED SOUTH AFRICAN SHALES

by

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ABSTRACT.

Some or all of the elements Li, Na, K, Rb, Cs, Mg, Ca, Sr, Cr, Mo, Mn, Fe, Co, Ni, Cu, Ag, Au, Zn, Pb and Tl are determined by Atomic Absorption Spectroscopy in soluble organic and total organic separates from thirty-six samples of South African carboniferous shales. The whole rock values for most of these elements in the samples are known and can be compared with the corresponding values of the organic fraction. A colloidal technique is developed to extract fairly pure kerogen from the shales. Rb, Cs, Ca, Cr, Co, Ni, Cu, Zn and Pb are concentrated in the organic fraction. The results for Rb, Cs and Ca are unexpected. The elements are apparently associated with a sub-fraction of the organic fraction. Several new organic geochemical parameters are developed to interpret the results. Interelement correlations in the various fractions of the shales, the relationship between metal content and organic content, the relationship between concentration of metals by organic matter and residence time, and the use of the metal content of the organic fraction as a paleosalinity test are discussed.

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1. INTRODUCTION.

1,1 GENERAL.

Danchin /1/ and Hofmeyr /2/ have recently been engaged in the analysis of South African shales. They suspected that there might be a correlation between the percentage loss of weight on ignition (PLOW) and the concentration in the whole rock of certain heavy metals. i.e. the greater the PLOW, the higher the whole rock concentration of e.g. Ni, Co and Mo in the shale. The inference was that the loss on ignition was due to combustible organic matter, and that the heavy metals were more concentrated in the organic fraction of the shale than in the inorganic. In all cases they destroyed organic material in the shale by ignition at 950°C and analysed the whole rock ash by x-ray fluorescence and/or optical spectrography.

The object of this project was to develope a method of physically separating the organic and inorganic fractions of the shale by some method which would not disrupt the elemental concentration in either fraction, to analyse the organic fraction for several metals, and to compare the results with the whole rock values. In this way, it was hoped, we could learn more about this suspected organic-heavy metal correlation. Correlations of this sort are important because of the enormous influence that organic compounds have on the geochemical distribution and movement of many elements in seas, streams, soils etc. /3, 31,32/

The organic separates are dealt with in two sections:

1) Benzene/methanol soluble fraction.
2) Total organic separates.

Twenty metals were determined in 2), and nine in 1), by Atomic Absorption Spectroscopy. (A.A.)

1.2 NOTES ON ORGANIC GEOCHEMICAL NOMENCLATURE.

The nomenclature of organic geochemistry is confused and ambiguous. /5/ For example, a very wide range of material has been labelled "kerogen" in the literature. Usually kerogen refers to insoluble caustobiolithic material. I have not studied the organic chemistry of my samples and cannot therefore define their organic content in terms of the nomenclature of other writers. For this work I define "humic" organic material or kerogen as that material typical of mature coal. i.e. it is sparingly soluble in any solvent, contains few simple compounds, is poor in free hydrocarbons, consisting instead of high polymers of C, H, O, N and other minor elements, and yields bituminous substances, (paraffins, aromatics and other minor compounds) by destructive distillation.

Similarly, bituminous caustobiolithic material is defined as those tarry substances similar to the organic material of petroleum or oil shale, which consist mainly of free long-chain (usually C_{10}) hydrocarbons, and are largely soluble in simple organic solvents. Amongst others, Forsman /16/ and Breger /5/ discuss organic geochemical nomenclature.

Organic remains in rocks can be divided into two major classes:

1) Acaustobiolithic (noncombustible) material, for example $CaCO_3$ and SiO_2 from shells and diatoms respectively. The non-organic elements associated with acaustobioliths are Ca, Mg, Sr, P and I /29/.

2) Caustobiolithic (combustible) material, e.g. kerogen, humic acids, petroleum and coal.

In my samples acaustobiolithic material is absent or all but absent. When I refer to organic matter, I mean caustobiolithic organic matter. This convention is general in the literature.

1.3 SOME GENERAL NOTES ON CAUSTOBIOLITHS AND ORGANO-METALLICS IN OLD SEDIMENTS.

In section (1.2) I mentioned the two broad groups (humic and bituminous) into which most of the caustobiolithic material of old sediments can be divided. I exclude from this discussion fresh organic material which has not yet decomposed or stabilized. Over geological time, unstable and water-soluble substances are destroyed, altered or removed. The bituminous group is unimportant in the shales I studied, and is present only in very minor amounts, compared to the humic. (See section on Results for the soluble fraction).

The humic materials are usually very complex in structure and have large, sometimes enormous molecular weights. According to Francis /4/ the molecular weights of approximately 80% of coal molecules averages about 3000 and much of the remaining 20% lies in the range 100,000 to 5,000,000.

Humic acids are remarkably stable, and are not decomposed chemically or biologically under non-oxidizing conditions. /3/ Because they are formed by a somewhat haphazard condensation of various organic (and sometimes inorganic) compounds released by the decay of different biological materials under various conditions, the elemental composition of humic materials shows wide variation. /4, 7/ According to Manskaya and Drozdova /6/ the structure consists largely of six-membered heterocyclic rings with various side chains, some five-membered rings, and various other functional groups and compounds which may be combined, complexed or absorbed to the humic molecule. Fig. R1, showing a theoretical chemical structure of coal is reproduced from their book. Fig. R2, from Francis /4/ shows a hypothetical structure for the vitrinite fraction of coal. Metal ions and even minerals can be strongly attached to this network. Thus metal chelates, organo-clay complexes and elemental carbon etc may find a niche in this rambling, cross-linked amorphous molecule.

Fig R.1.

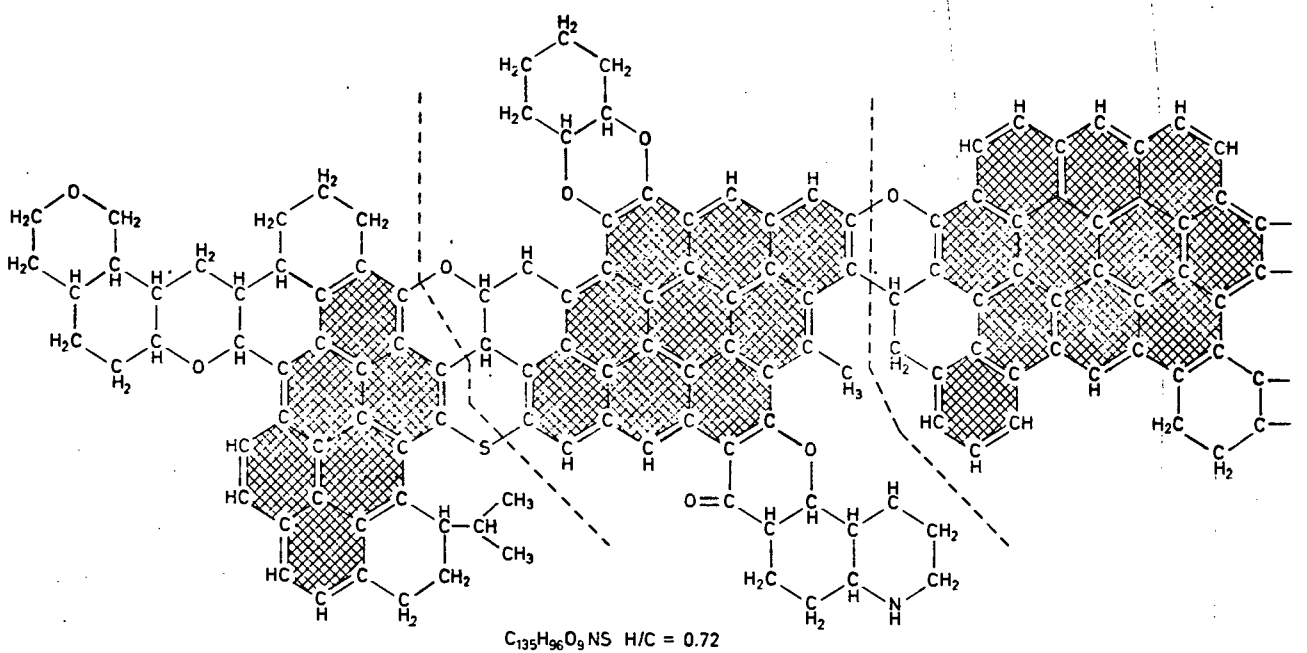


FIG. 34. Model of chemical structure of coal according to Fuchs and van Krevelen (van Krevelen, 1957).

Fig R.2

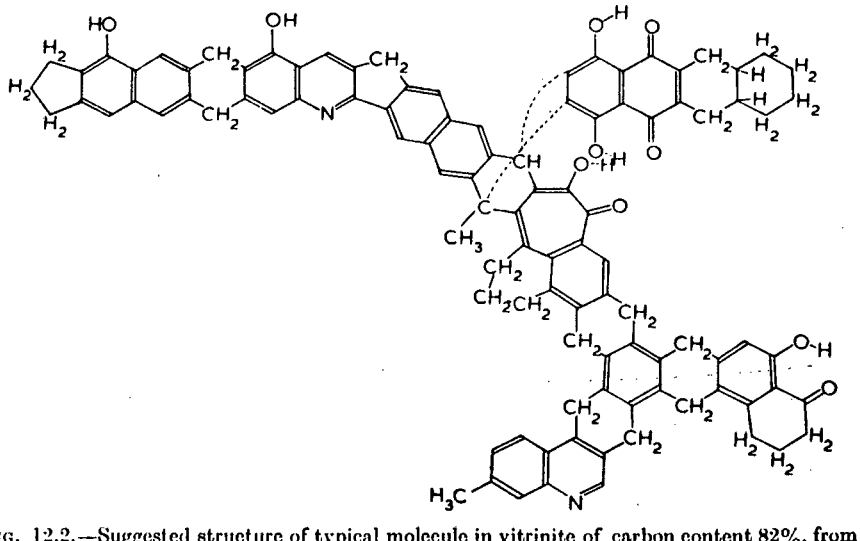


FIG. 12.2.—Suggested structure of typical molecule in vitrinite of carbon content 82%, from Given, ref. 41.

Forsman /7/ and Swain /8/ give a detailed account of the chemistry and geochemistry of humus and kerogen for the interested reader. The related topic of coal geochemistry is adequately covered by Francis /4/ and Van Krevelen /9/.

Unfortunately, it is beyond the scope of this project to go deeply into the organic chemistry of kerogen, or the physical chemistry of the organo-metal-mineral association. Studies of this sort require sophisticated modern instruments. Hood et al /31/ gives an excellent account of the use of techniques such as Electron Spin Resonance and laser Raman spectroscopy in the analysis of organo-metallic compounds.

It must suffice to say that this organic matter can be expected to be, and is, a powerful metal complexing agent. /3, 4/ Fig. R3, from Manskaya and Drozdova shows the relationship between the metal and humus contents of soil. The importance of this complexing ability is stressed when one notes that the mass of carbon held in living organic (-C-C-) bonds in the biosphere is estimated at 7×10^{11} tons /3/ and that in dead humic material even greater, 60×10^{11} tons /3/ The main source of humic materials is lignin, /3/ from which it derives its polycyclic skeleton.

My object was to see to what extent this complexing activity has influenced the distribution of various metals in the organic and inorganic fractions of the sediments I studied.

Fig. R.3.

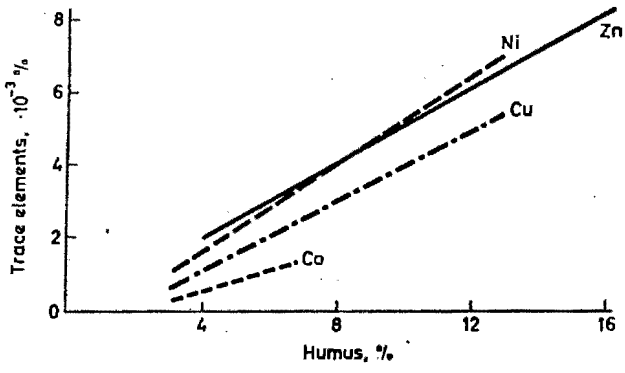


FIG. 41. Relationship between humus content of soil and trace elements.

1.4 SAMPLE ORIGIN AND DESCRIPTION.

The samples are all fresh shales from boreholes or coal mines in the Karroo and elsewhere. The LDW/WB samples are from the White Band of the Dwyka Series of the Karroo System. The JP sample is from the Jeppestown Series of the Witwatersrand System. The rest are from the Northern Facies of the Ecca Series (i.e. Permian Coal Measures) of the Karroo System.

The mineralogy of the samples is broadly similar. The inorganic fraction consists of from 50 to 95% of the whole rock. Kaolinite (50-80% of inorganic substances) predominates, followed by Quartz, 5-15%, Illite, sometimes calcite, iron compounds and minor minerals. These samples are described in great detail by Danchin /1/

The organic material is invariably black and colours the whole rock powder black or dark grey in most samples. When separated, it looks like powdered coal, and is similar to kerogen from many other localities described in the literature. /4,6,7,16/

When heated, it glows and burns like coal, smells like burning coal and leaves a yellow or red ash like coal. Only a small percentage (approximately 1%) of the total organics is soluble in simple organic solvents. The best solvent found was benzene/methanol. It is pyrobituminous, i.e. when heated in a closed tube, it yields tarry substances. Under the microscope, it is black, amorphous, opaque and uninteresting. When nearly free of mineral matter, it gives no meaningful X-ray diffraction trace.

By these criteria, I classify this organic matter humic or coal-like, and non-bituminous. I believe it can be broadly regarded as a comminutated coal, diluted by mineral matter. Many of the samples were collected near workable coal seams. /1/

2. INVESTIGATION OF THE TRACE ELEMENTS IN THE SOLUBLE ORGANIC FRACTION.

2.1 GENERAL DESCRIPTION OF THE METHOD.

The soluble organic compounds are removed by prolonged ultrasonic extraction of the finely crushed rock with 9:1 v/v benzene/methanol to which is added some NH_4OH. This method is unconventional. Usually the material is refluxed. Hunt /15/ describes conventional extraction methods. The extract is filtered, oxidised, taken up in solution and analysed by A.A. Tests showed the optimum extraction time to be 48 hours. Ten samples were analysed for nine metals.

2.2 PREVIOUS WORK IN THIS FIELD.

The extraction of soluble organic compounds from rocks or natural waters is widely described in the literature. /4, 12, 13, 31, 32/ However, few of these authors are interested in the metal content, and most of the work is on petroleum, not kerogen.

Manskaya and Drozdova /6/ summarize most of the available literature, much of which is in Russian. Ciuffolotti et al /10/ analysed oils and asphalts for trace elements by Neutron Activation techniques. Hanya and Ogura /11/ used ultraviolet spectroscopy to examine dissolved organic material in water.

Relevant papers will be mentioned as I go. where ?

2.3 EXPERIMENTAL DETAILS.

Separation and Analysis.

1) All materials were Analar or equivalent.
2) About 10gm of finely powdered (120 mesh) shale was accurately weighed into a 250ml conical flask.
3) 200ml 9:1 v/v benzene/methanol and 2ml NH_4OH were added.
4) The flask was placed in an ultrasonic tank for 48 hours, and benzene/methanol was added, when necessary, to compensate for evaporation. The flask was regularly shaken because the material slowly settles out. After a few hours the temperature of the water in the tank stabilizes at about 65°C.
5) The suspension was filtered under vaccuum.
6) The filtrate was evaporated to dryness or to a tarry residue.
7) 25ml of concentrated nitric acid was added, and the mixture evaporated to dryness. This destroys most of the organic matter.
8) When the flask had cooled, 25ml of perchloric acid was added and the temperature gradually raised to drive off all $HClO_4$. This destroys resistant organic compounds.
9) The residue was taken up in 10% HCl.
10) This solution was analysed. The proceedure for A.A. is described in the section on Total Organics.
11) A blank of 30% Quartz, 30% Illite, 30% Kaolinite, 5% Calcite and 5% Fe_2O_3 was run.

2.4 RESULTS.

Solubility.

I found the soluble fraction to be about 0.5 to 2% of the whole rock by weight. Hunt /15/ found that in shales he studied this figure is lower, viz 0.1 to 0.5%. He states that many authors have found that the percentage of the total caustobiolithic carbon of shales in soluble compounds is commonly from 3-7. Forsman and Hunt /16/ give the soluble fraction in a group of sedimentary rocks of marine origin as 5-15% of the total organics. Generally this material resembles petroleum.

Trace Elements.

The results for ten samples and nine elements are recorded in Table A, which has an accompanying explanation. The results are recorded in terms of the percentage of the organically bonded element which is extractable with 9:1 v/v benzene/methanol under the conditions described in section 2.3. For example, take the Fe value for GB48/65/12, which is 10.0. This means that of every 100 Fe atoms in that sample which are organically bound, (apparently) 10 of those atoms can be removed by the benzene/methanol solvent. I say apparently because the benzene/methanol extracts Fe from the inorganic fraction too. (See Discussion of Results.) In theory, this percentage is totally independent of the inorganically held iron. In practice, some of those ten atoms are extracted from the minerals.

TABLE A % OF ORGANICALLY BOUND ELEMENT THAT IS SOLUBLE.

	Zn.	Fe.	Cu.	Mn.	Mg.	Ca.	Li.	Tl.	Rb.
SEC26	Cont	BDT	Cont	BDL	Neg	BDL	BDL	BDL	BDL
SEC25	9.2	Neg	BDL	BDL	Neg	BDL	BDL	BDL	BDL
A78/4	Cont	BDL	BDL	Neg	Neg	80.2	BDL	BDL	BDL
A78/9	14.7	Neg	39.6	BDL	Neg	90.3	BDL	BDL	BDL
A62/5	10.6	7.7	25.4	Neg	Neg	Neg	BDL	BDL	BDL
EC.11	Cont	11.9	Cont	8.1	Neg	17.1	BDL	BDL	BDL
EC.16	Cont	5.3	Cont	Neg	Neg	Neg	BDL	BDL	BDL
GB45/65/10	Cont	Neg	Cont	Neg	Neg	Neg	BDL	BDL	BDL
GB48/65/12	Cont	10.0	Cont	Neg	Neg	Neg	8.4	BDL	BDL
WC5B	NDet	Neg	NDet	4.8	35.4	50.7	BDL	BDL	BDL

Explanation of Table A.

Cont = Insoluble organic fraction contaminated by Cu, Zn, Pb.

NDet = Value cannot be calculated because whole rock value has not been determined.

BDL = Value is below the detection limit.

Neg = The theoretical concentration of the element in the organic matter is negative. See section on results for the total organic fraction.

2.5 DISCUSSION OF RESULTS.

The results for the soluble fraction are few in number. Only a few elements and samples were selected, at random, mainly as a pilot study. The number of results has been reduced even further because of:-

1) contamination (referred to in section 3.5),
2) the fact that the theoretically calculated value of 'PER', which is needed to calculate Table A, is often negative. (See section 3.5)
3) In many cases, the metals were not detectably concentrated in the benzene/methanol fraction.

It appears, however, that the proportion of extractable organically bonded metal varies between elements. The approximate values are:-
Zn 10%, Li 8%, Fe 8%, Cu 30%, Mn 5%, Mg 35% (one sample only) Ca 17-90%.
The elements Tl and Rb were not detectable in any extract and so I cannot comment further on these elements. Let us define this parameter as the "PEOB" of the metal (from Proportion of Extractable Organically Bonded metal)

In the following discussion, I use Zn only as an example. The theoretically determined PEOB values given in Table A and summarized above, are calculated from:-

1) The A.A. analysis of the soluble extract which, in the absence of upsetting factors, gives the amount of "soluble Zn" (i.e. Zn held by soluble organic matter) as a percentage of the total Zn in the whole rock.
2) "PER" from the section on the total organics, which is a measure of the "total organic Zn" (i.e. the total Zn held by soluble and insoluble organic matter).

The PEOB values of Table A are then a measure of the ratio of "soluble Zn" to "total organic Zn" expressed as a % of "total organic Zn"

This calculation is only valid if:

1) No Zn is extracted from the minerals. I think the blank eliminates this possibility. The blank is not representative of the samples, but it does give all the minerals present a chance to contaminate the benzene/methanol with trace metals.

2) No Zn is extracted from the insoluble organic matter.

Let us assume that the average sample has 30% total organic matter by weight and 1% soluble organic matter by weight. Then the soluble matter is 3.3% of the total organic matter, on average. Let us assume (as we may reasonably do from the results of section 2.4) that the range is about 2-7%. If we ignore the interferences mentioned above, then the PEOB of Zn, Li, Fe and Mn (all low) indicate that the proportion of these metals in the soluble fraction is equal to or slightly higher than the proportion in the total organics. For the elements with high PEOB (Cu, Mg and Ca) the concentration of these metals in the soluble fraction is anything from 4 to 45 times the concentration in the total organic fraction, and one begins to wonder if this increase is real, or whether the previously mentioned loss of ions from the insoluble organic fraction is masking the true values.

At present I can only speculate as follows: Cu is apparently firmly held by humic material, and Mg and Ca less firmly. (See section 4) All three are probably firmly held in the organic fraction, since they are not significantly extracted from the blank. It seems to me then, that the high Cu PEOB may be real, but that the high values for Mg and Ca are due to extraction of these metals from the insoluble organic fraction by the solvent.

2.6 CONCLUSIONS.

Although these results are too few in number to be statistically meaningful as an estimate of the proportion of soluble organometallics in the samples, I feel that they do demonstrate the important point that, for the elements studied, the maximum extraction of inorganically held metal by the organic solvents themselves is quite low. Naturally, I cannot extend this conclusion to the other elements determined in the section on the insoluble organic fraction. I have assumed that they behave similarly.

3. INVESTIGATION OF THE TRACE ELEMENTS IN THE TOTAL ORGANIC FRACTION.

3.1 GENERAL DESCRIPTION OF THE METHOD.

The shale is very finely ground in a mortar machine in a slurry of Ammonia solution, and afterwards mixed with benzene. The mixture is subjected to ultrasonic bombardment. The immiscible organic and aqueous layers are separated. The benzene layer contains most of the soluble and insoluble organic material which is recovered and analysed for twenty metals by A.A.

WARNING:

Do not, under any circumstances, use benzene or any inflammable organic compounds in the mortar machine. My attempt to grind in a benzene/NH_4OH mixture resulted in a serious explosion, presumably detonated by electrical sparking.

3.2 PREVIOUS WORK IN THIS FIELD.

Several authors have commented on the positive relationship between the carbon content (or organic content) and the concentration of various metals in many natural materials, e.g. shales, humus, coal, petroleum and soils and an extensive literature exists on the subject. An excellent and comprehensive summary is given by Manskaya and Drozdova /6/. For example, Wedepohl /26/ found a definite relationship, in the Kupferschiefer of North Western Germany, between caustobiolithic carbon and V, Cr, Ni and to a lesser extent Mo. Fig. R4, shows the relationship between the elements Cr and Ni, and the carbon content of samples from the Kupferschiefer /26/. He notes similar occurences in other bituminous shales.

Curtis /28/ found that V, Cr, Mn, Ni, Co, Cu, Mo and U are closely correlated to the organic carbon content of many shales, whereas B is inversely related, and Sr and Ba are indifferent to the organic content.

However, very few analyses of separated kerogen are recorded and as far as I know this is the first time that South African shales have been analysed in this manner.

At the beginning of this project, I tried to separate organics using froth flotation techniques as described by Degens et al /17/ and most of my research into the literature was along this line, which proved to be unsatisfactory for my purposes. Degens and his co-workers ground the samples to 10 microns in a ball mill, and used mineral oil as a collector and pine oil as a frother. Some of their results for the analysis of shales and organic fractions separated by froth flotation are given in Fig. R5.

Fig R4.

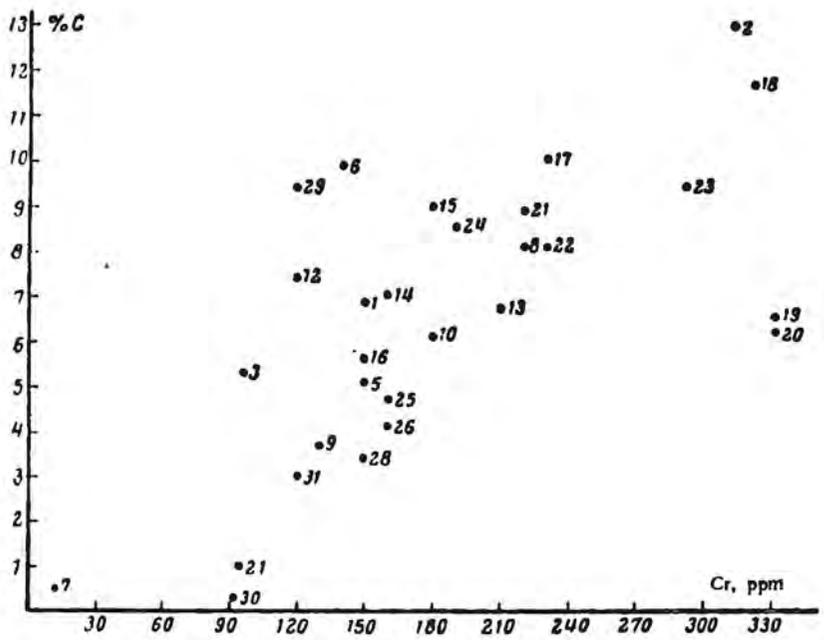


FIGURE 3. Dependence of concentration of Cr on carbon content in the Kupferschiefer deposits. Indications as in Figure 2.

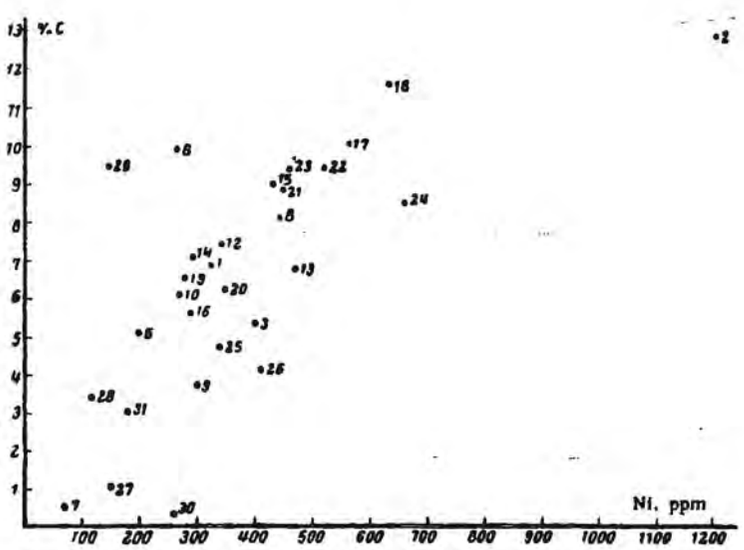


FIGURE 4. Dependence of concentration of Ni on carbon content in the Kupferschiefer deposits. Indications as in Figure 2.

Fig R5.

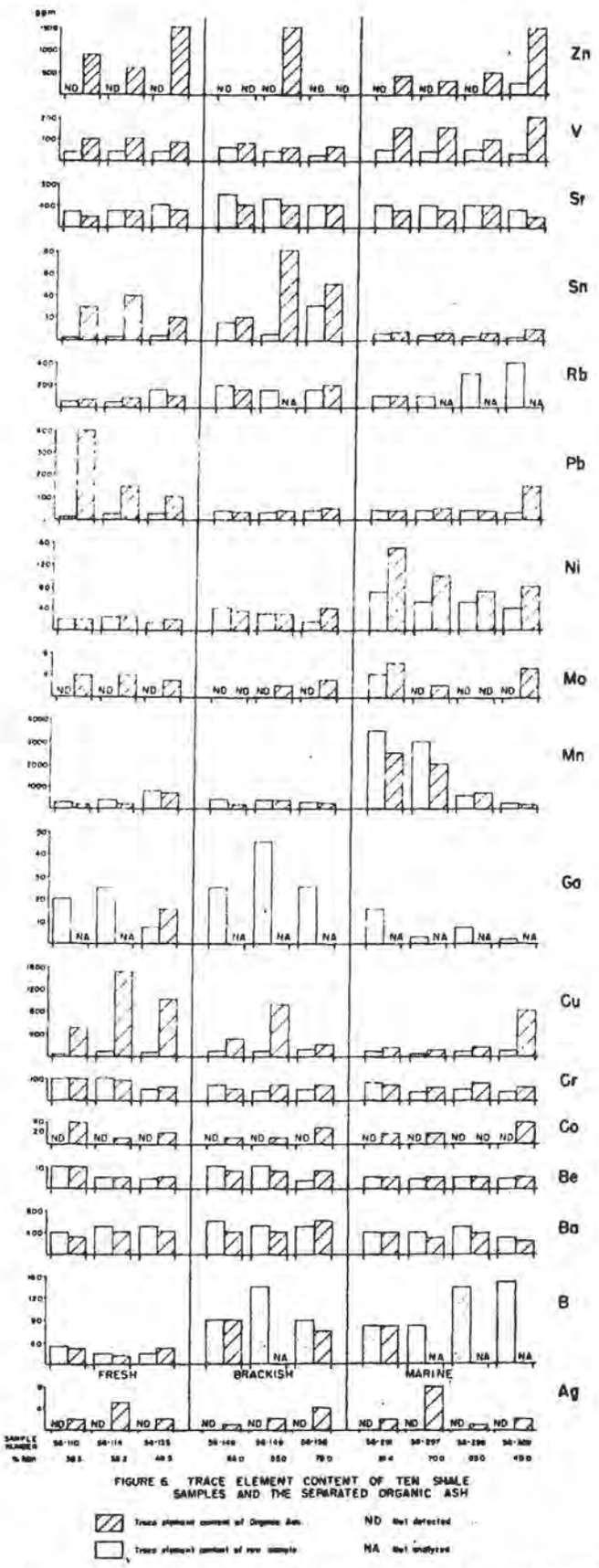


FIGURE 6. TRACE ELEMENT CONTENT OF TEN SHALE SAMPLES AND THE SEPARATED ORGANIC ASH

FIG. 6.—Trace element content of ten shale samples and the separated organic ash.

I encountered the following difficulties in my experiments on flotation:-

1) Lack of sophisticated flotation equipment.
2) Lack of an effective flotation agent (I found pine oil unsatisfacotry).
3) The high metal content of most natural oils.
4) The difficulty of removing these oils from the sample afterwards.
5) Many of my samples would not respond at all to flotation, or else the flotated material contained much clay, which could not be removed.

While working on froth flotation techniques, I developed the colloid technique as a sideline and, more by accident than design, it proved to be the answer. Subsequently I found that a similar technique had been developed by Duel in 1956. /18/

Duel used a ball mill and paraffin. I believe my technique to be superior in several ways: percentage separation is better, it requires less time (his samples were ground for about 300 hours), no washing is required, (reducing trace element losses) smaller samples are needed and there is less metal contamination.

Francis /4/ reports that density and electrostatic methods for separating kerogen have been developed.

Forsman and Hunt /16/ separated humic materials from shales by destroying mineral matter with HF, HCl, or Zn digestion. I think that this violent chemical treatment is sure to drastically disturb the trace element content of the organic fraction. Szalay /3/ has demonstrated that HCl removes cations from humic acids, and that these are not reabsorbed at a pH below 3.

The standard proceedures for analysis are given in the handbook for the instrument. /48/ These have been elaborated by Orren. /47/

Any relevant papers will be referred to as I go.

3.3 EXPERIMENTAL DETAILS.

Method of Separation.

The samples used had previously been ground for conventional major and trace element analyses. /1/ They were broken, crushed to 120 mesh and stored.

I treated them as follows:

1) All materials used were "Analar" or equivalent purity.

2) About 5gm of shale was weighed into the agate of a mortar machine. I used a machine supplied by Agate and General Stonecutters London (Type No 7513). The powder was wetted with dilute ammonia solution (1 conc. NH_4OH : 3 H_2O) and ground for three hours at medium speed. A few drops of the dilute NH_4OH solution were added now and then to compensate for evaporation.

3) This sludge was transferred to a 500ml separating funnel, to which was added 200ml H_2O, 25ml conc. NH_4OH and 100ml benzene. The flask was vigorously shaken, causing most of the organic material to complex with the benzene and float as a black scum.

4) The flask was transferred to an operating ultrasonic bath (Dawe Ultrasonic Cleaning Tank). The flask was moved around in the tank to find the optimum resonance position. In this position, the floating sludge shivered or "hummed" very intensely. (i.e. high frequency oscillation but little disruption). Under these conditions, a white "snow" of inorganic material (mainly clay) separated from the scum and collected at the scum-water interface. By jerking the flask suddenly (this is difficult to describe, but easily demonstrated) the "snow" was propelled into the aqueous layer where it remained. This process was repeated until no more snow separated. This often took an hour or more.

5) The aqueous layer was separated, and the flask charged with dilute benzene/ammonia as before. Ultrasonic treatment was repeated until a limit was reached when the organic matter began to break up and disperse into the aqueous layer.

This limit, in terms of maximum obtainable PLOW, varied considerably from sample to sample. The aqueous layer was separated.

6) The benzene-sludge layer was collected and evaporated to dryness in a pyrex bowl in an oven.

7) About 1gm of the dry organic fraction was weighed into a flat silica crucible and ignited in a muffle furnace at 720°C for 24 hours. The crucible was weighed after cooling in a desiccator.

8) About 0.1-0.3 gm of ash was accurately weighed into a platinum crucible and dissolved in a mixture of 10ml $HClO_4$ and 10ml HF. The mixture was evaporated to dryness and the dissolution repeated if any solid material remained.

9) The contents of the crucible were dissolved in 10ml conc. HCl and transferred quantitatively to a 50ml volumetric flask by flushing with water.

10) The solution was stored in a clean, acid rinsed, polythene bottle.

11) A reagent blank was run.

Method of Analysis.

A Perkin-Elmer 303 Atomic Absorption Spectrometer /48/ with Hitachi Recorder Readout was used. The conditions are given in Table B. Most of the elements were determined straight from the polythene bottles mentioned in 10) above. Standards were prepared from pure reagents in water. However, a measured aliquot from the polythene bottles was removed and buffered for the determination of Cs, the alkaline earths, and the elements requiring a nitrous oxide flame. This buffered solution contained 1000 p.p.m. La and 1000 p.p.m K to reduce interference and to enhance sensitivity. The standards for these elements were similarly buffered.

No special precautions were taken, but according to Dr M J Orren, who supervised the analyses, the precision (approx 3.5%) and accuracy are acceptable for the nature of the project, which is to demonstrate trends rather than to establish absolute values.

In any case, the analytical precision is much higher than the precision of the separation technique, which, in terms of percentage loss of weight on ignition, is only about 10%.

TABLE B. DATA FOR ATOMIC ABSORPTION SPECTROSCOPY.

Element.	Li.	Na.	K.	Rb.	Cs.	Mg.	Ca.	Sr.	Cr.	Mo.	Mn.	Fe.	Co.	Ni.	Cu.	Ag.	Au.	Zn.	Al.	Pb.
Burner		Ss	L&S	L	L	Ls		L	L	L	L	S	L	L	L	L				L
Burner Height			3	.1		0.2			-	-	-	-		-	-	-				-
Air Flow		4	4	9		5	9	9	7.5	6	9	5	9	9	8	9	8			9
Gas		A	A	A	A	A	A	A	A	N	A	A	A	A	A	A	A	A	N	A
Gas Flow		4	4	9		5	9	9	9.0	10	9	8	9	9	9	9	8			9
Wave Length		295? 589	383?		426	285	212	230	358	314	280	248	241	232		328				283
Slit	')	4	4	5	5	4	4	4	4	5	4	4	4	3		4	5			4
Gain		3.0	5.8	4.8	6.1	5.2	5.3	5	5	4.8	5.9	5.2	5.5	5.6		5	4			5.1
Lamp Current	',				11	8	2		10	15	10	10	10	14		4	10		14	5
Recorder Expansion					10	1		3	10		3	1		10			10		3	
Noise Suppression						1					3						3		3	10
Comments	STD	STD	STD	STD	FIL					OPT		OPT			STD	OPT		STD	OPT	

NOTES:-

STD = Standard conditions as per manual.
FIL = Filter in. (?)
OPT = Optimized on recorder.
L = Normal long path burner (as) ytha.?
Ls = Long path burner sideways. as ytha.?
S = Short path burner ?
Ss = Short path burner sideways.?

A = Acetylene
N = N2O. ?

3.4 THEORY OF THE METHOD.

Duel /18/ describes the separation process as being an adaption of the Trent Process, used for freeing powdered coal of mineral matter. The effectiveness of the separation technique depends on the number of free particles in the slurry, and hence fine grinding is essential. This attrition scrubbing also tends to remove the coat of organic matter adhering to the mineral grains.*

Degens et al /19/ used an electron microscope to detect the presence of this coat or film. The results are shown in Plate 1, reproduced from his article. They show clay particles which have been treated with oxidizing agents and one which has not. The results are not final proof, but they seem to indicate the presence of an organic film on the untreated particle, which, being amorphous and poorly diffracting, fuzzes the edge of the crystal.

Assuming that Degens et al /19/ are correct, it is easy to understand why grain size is important. See Figs 1A and 1B. Fig 1A represents a grain coated with an organic layer. If the benzene manages to hold this heavy particle, it will introduce a large amount of inorganic material into the organic fraction. But, if this particle is ground and subjected to a scrubbing action, a collection of particles as in Fig 1B results. Most of the particles will be either purely organic (a) or purely inorganic (b), and only a few, corresponding to the interface zone of Fig 1A will be composite (c). Hence a better separation is obtained, because less inorganic matter is carried into the benzene layer. The surface activity of the ammonia is important here in suppressing the flocculation of (a) and (b) particles.

Once separated, the mineral and organic grains can be isolated in two colloid systems.

* Keith. M. L. Private Communication.

Fig 1A.

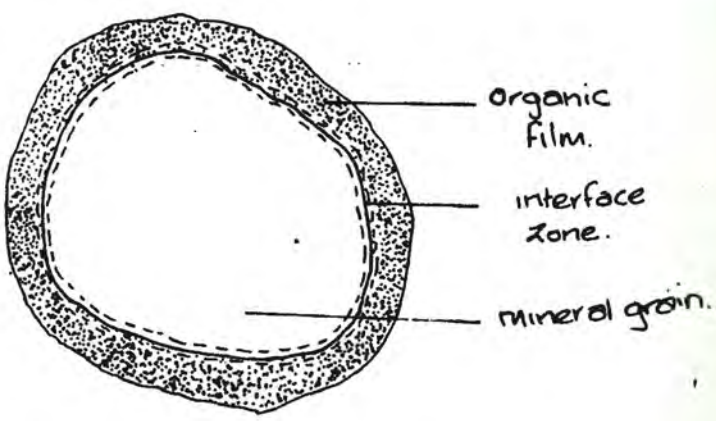


Fig 1B.

The non-polar organic material becomes suspended in, or attached to, the non-polar benzene, while the polar minerals prefer the polar aqueous layer, because the atomic symmetry of polar compounds leaves unbalanced electrical charges which tend to rotate the molecule in an electrostatic field. /18/ This is the principle of most flotation processes. /18/

The hydrosol and organosol fractions are easily separated, because they are immiscible. The separation process is shown schematically in Fig. R6, from Duel's paper. Naturally this process is not perfect, and ideal separation is not achieved. The problem of preferential flotation or leaching of certain minerals by the benzene is dealt with elsewhere in this work.

I believe that the success of this method depends largely on the presence of the ammonia, which has surface active properties. Ammonia was used because it worked better than all of the many detergent chemicals I tried and because it is easily obtained in a very pure grade.

I do not know what the action of the ammonia is. However, the following points, gleamed mainly from Moillet /20/, may be significant:

1) The surface active agent (S.A.A.) is absorbed at the interface of the newly broken crystal surface, preventing reagregation and flocculation.

2) The S.A.A., by wetting the crystal surface thoroughly, removes all traces of air from the surface, ensuring maximum mechanical contact.

3) By lowering the surface tension at the solid-liquid interface, less work is required to disrupt the particle. Hence particles which would previously have excaped with only a straining, will now be disrupted since they have lost the "elastic cushion" protection of the surface tension.

4) Some particles which are not disrupted by a particular set of forces bearing on them, are nevertheless strained, and strain cracks may appear. Normally these would heal spontaneously when the stress is removed. However, the S.A.A. may enter the crack, keeping it open and at the next impact the grain has a reduced chance of survival.

Fig. R6.

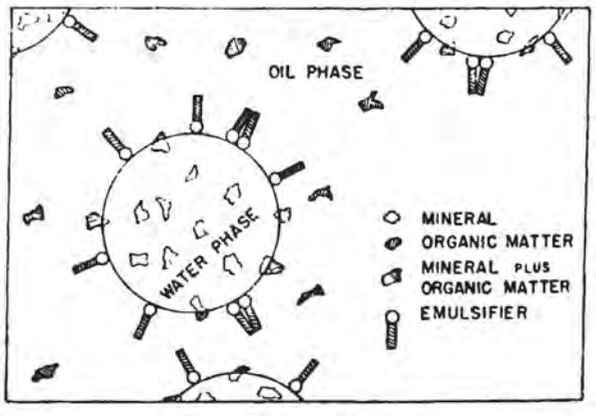


FIG. 2.—Water-in-oil emulsion.

The result of these factors is a greater disruption in unit time if a S.A.A. is present. This can be represented quantitatively as follows: Assuming that the rate of disruption of a species of particles (of a specific size, shape, composition etc.) is directly proportional to the number of these particles present. Then:

$$dZ/dt = -kZ$$

where Z is the number of particles at time t and k is the milling efficiency constant. Integration gives

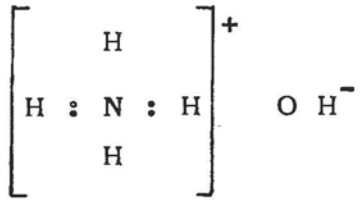
$$\ln Z = \ln Z_o - kt$$

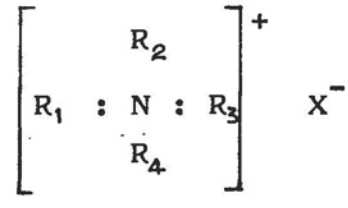
where Z_o is the number of particles at time t = zero. To reduce Z to zero with absolute certainty would need a time t = infinity. But to reach some maximum permissible value of Z (say 5% of Z_o) a finite time t′ is needed given by

$$t' = (\ln Z_o - \ln Z')/k$$

where Z′ is the permissible value of Z.
It has been shown experimentally that S.A.A's can often drastically increase k, with a resulting sharp decrease in t′. Assuming that no other factors are involved, this may explain the discrepancy between Duel's grinding times (300 hours) in the absence of S.A.A's and mine (3 hours).

Ammonia is the "parent" of an important group of cationic S.A.A's. /20/ Compare the structures of Ammonia and a generalized quaternary ammonium compound.





3.5 RESULTS.

The results for the total organic separates are given in Tables C, 1-20, 21-37, 21A-37A, 25B, 25C, 38-43 and 44-52; and Figures 2-18, 19-33 and 33A, all of which have accompanying explanations. These comprise frequency distribution diagrams, analytical and theoretically estimated results, correlation coefficients and graphs. They are in this order:-

1) PLOW data.
2) Analytical.
3) Element Correlations.
4) Relation between PLOW and metal content.

EXPLANATION OF TABLE C.

The PLOW Table C is largely self explanatory. It expresses the percentage loss of weight on ignition of the whole rock and the separated fraction, together with the ratio of the two PLOW values. The mean of this ratio is 5.04. Samples 37 and 38, given by way of comparison, are the inorganic separates corresponding to samples 2 and 14. They show a reduction of the organic content of the inorganic fraction.

TABLE C.

DATA RELATING TO LOSS OF WEIGHT ON IGNITION

ORGANIC FRACTION

REF	SAMPLE	WHOLEROCK PLOW	WHOLEROCK ASH	FRACTION PLOW	FRACTION ASH	PLOW RATIO
1	A62/2	33.06	66.94	92.31	7.68	2.79
2	A62/5	21.92	78.08	81.67	18.32	3.72
3	A76/3	38.60	61.40	91.95	8.04	2.38
4	A76/5	20.19	79.81	81.65	18.34	4.04
5	A76/6	36.77	63.23	72.14	27.85	1.96
6	A78/3	40.20	59.80	91.21	8.78	2.26
7	A78/4	20.29	79.71	95.48	4.51	4.70
8	A78/9	24.06	75.94	68.95	31.04	2.86
9	A78/10	24.90	75.10	77.60	22.39	3.11
10	A78/11	44.53	55.47	93.26	6.73	2.09
11	AEC 1	23.17	76.83	52.44	47.55	2.26
12	BEC 4265	27.52	72.48	47.64	52.35	1.73
13	BEC 4270	17.16	82.84	46.25	53.74	2.69
14	EC 7	16.06	83.94	91.87	8.12	5.72
15	EC 11	16.63	83.37	52.86	47.13	3.17
16	EC 15	37.28	62.72	77.85	22.14	2.08
17	EC 16	30.29	69.71	50.82	49.17	1.67
18	EC DAN 3	13.83	86.17	84.03	15.96	6.07
19	EC DAN 5	18.06	81.94	75.69	24.30	4.19
20	GB45/64/7	12.81	87.19	80.72	19.27	6.30
21	GB45/64/10	11.54	88.46	63.59	36.40	5.51
22	GB47/64/8	11.53	88.47	63.40	36.59	5.49
23	GB47/64/10	13.02	86.98	85.66	14.33	6.57
24	GB48/65/5	13.32	86.68	95.02	4.97	7.13
25	GB48/65/9	16.70	83.30	91.15	8.84	5.45
26	GB48/65/12	27.86	72.14	96.31	3.68	3.45
27	SEC 1	15.54	84.46	88.37	11.62	5.68
28	SEC 9	14.39	85.61	47.55	52.44	3.30
29	SEC 13	25.63	74.37	69.36	30.63	2.70
30	SEC 25	9.53	90.47	31.06	68.93	3.26
31	SEC 26	9.65	90.35	56.10	43.89	5.81
32	WEC 5B	3.46	96.54	61.61	38.38	17.80
33	WEC 5C	5.43	94.57	52.88	47.11	9.73
34	LDW3WB	10.19	89.81	92.01	7.98	9.02
35	LDW4WB	8.88	91.12	23.92	76.07	2.69
36	JP 5	2.44	97.56	54.55	45.44	22.35

INORGANIC FRACTION

37	EC 7	16.06	83.94	13.71	86.28	0.85
38	A62/5	21.92	78.08	16.12	83.87	0.73

EXPLANATION OF TABLES 1 - 20, AND D.

Tables 1-20 contain the results of the A.A. analyses, and certain theoretical parameters calculated for the samples from these results and from the results of Table C. The following notes should make the meaning of these tables clear:-

1) Ref. is merely a reference number for comparing the same sample in various tables.

2) X is the concentration in the analysed solution. Where the element is not sufficiently concentrated to be detected, this is indicated by an inequality and the detection limit for the element under the conditions of the analytical run. Because the computer now uses the detection limit rather than the true value of X in its calculations, these inequalities are extended to all other values except Cw.

3) Cw is the whole rock value from Danchin /1/ and Hofmeyr /2/. Where not determined, a dash is written. Without Cw, the data given in the columns to the right of Cf cannot be calculated.

4) Cf is the concentration, calculated from X, of the element in the organic-rick fraction separated from the whole rock.

5) CwCf is the ratio Cw/Cf.

6) Using the PLOW data from Table C, and assuming that these data can be taken as the percentage of organic matter, and knowing Cw and Cf, a simple simultaneous equation can be formulated to calculate what the theoretical concentration in the organic fraction would be if the PLOW was 100. i.e. if we had eliminated all inorganic matter. Similarly, we can calculate a theoretical concentration of the element if PLOW was zero. i.e. if the sample had no organic matter in it.

Co, then, is the calculated concentration of the element in a theoretically pure organic fraction. i.e. PLOW = 100, and is given by:

$$Co = \frac{(100Cw - AwCi)}{Pw}$$

Where Aw is (100 - Cw) i.e. whole rock ash.
Pw is the measured PLOW for the whole rock.
and Ci is given in column 6 of Tables 1-20.

Naturally, this value must not be taken too seriously, since a 100% loss of weight would leave nothing to analyse! Nevertheless, it is a useful theoretical estimate of the concentration of the element in the organic matter.

Ci is the opposite to Co, i.e. the concentration of the element at PLOW = 0, corresponding to a theoretically pure inorganic fraction. It is subject to the same limitation as Co. It is given by:

$$Ci = \frac{100\ (PwCf - PfCw)}{(PwAf) - (PfAw)}$$

Where Cf is the concentration in the separated fraction given in column 5 of Tables 1-20.
Pf is the fraction PLOW from Table C.
and Af is 100 - Pf i.e. the fraction ash from Table C.

7) CoCi is the ratio Co/Ci.

8) PER is an estimate of how much of the element in the whole rock sample is held in organic compounds, expressed as a percentage of the total. It is given by:

$$PER = PwCo/Cw$$

9) Table 10, for Molybdenum, demonstrates an important point which should be borne in mind when examining the other tables. Because of the very low sample weights, dilution factors become very important. In table 10, it can be seen that all X values are below the detection limit, for the run, of 0.5 p.p.m.

Thus the corresponding calculated values of Cf are all maximum values. They are all rather high, and some are ridiculous. e.g. a detection limit in the sample of nearly 6000 p.p.m. in the case of sample 36 (JP5).

I regard the following samples as being subject to too great dilution to give reliable results:
Refs. 7, 13, 15, 16, 25, 31, 32, 33, 34, 35, 36.

It follows that these samples may be expected to give peculiar values in Tables 1-20, but in fact only two of these samples (BEC4270 and JP5) appear in the table of "extreme values" given in 10) below.

10) Table D is a summary of Extreme Values, which seem to me to be extreme in relation to the other values. These may be due to real variations, or to some analytical error. A few samples (SEC25, EC16, BEC4165 and A76/6) give extreme values for many elements. This is probably due to either a weighing error or a serious difference between the PLOW and the real organic content. The values for all elements for these samples should be held in suspicion.

11) Samples 37 and 38 are related to samples 2 and 14 in Tables 1-20. They are the corresponding inorganic rich fraction isolated from the aqueous layer (See section on Experimental Details). They are added for comparison with the organic fraction values, using columns Cw, Cf and Cw/Cf. The values in the other columns for samples 37 and 38 are meaningless, since they are calculated in terms of organic enrichment, and should be ignored.

12) At a late stage in this work I found that one of the brass holders of the agate of one of the mortar machines was causing contamination. This affected only those samples which were ground in that agate. Fortunately, I kept a record of these samples, which gave ridiculous Cu - Zn - Pb values. Pierre Hofmeyr and I analysed scrapings from the holder by Optical Spectroscopy. It consisted mainly of Cu, with Zn and Pb in amounts greater than 10%. A few other metals were present, but only in trace amounts. The affected samples are underlined in the Cu, Zn and Pb tables, and should be ignored.

TABLE 1 LITHIUM

REF	SAMPLE	X	CW	CF	CWCF	CO	CI	COCI	PER
1	A62/2	0.067	96.000	4.794	20.022	-7.033	146.885	-0.047	-2.422
2	A62/5	0.077	80.000	14.882	5.375	-5.084	103.886	-0.048	-1.393
3	A76/3	0.056	74.000	6.110	12.109	-4.127	123.116	-0.033	-2.153
4	A76/5	0.099	92.000	12.897	7.133	-10.708	117.982	-0.090	-2.349
5	A76/6	0.070	61.000	5.102	11.956	-38.902	119.095	-0.326	-23.449
6	A78/3	0.102	58.000	5.917	9.802	-3.047	99.038	-0.030	-2.112
7	A78/4	0.010	54.000	4.911	10.994	1.964	67.245	0.029	0.738
8	A78/9	0.254	59.000	16.418	3.593	-13.019	81.817	-0.159	-5.309
9	A78/10	0.169	62.000	12.419	4.992	-8.653	85.425	-0.101	-3.475
10	A78/11	0.039	57.000	3.096	18.409	-4.348	106.249	-0.040	-3.397
11	AEC 1	0.148	20.000	9.060	2.207	-8.711	28.658	-0.303	-10.091
12	BEC 4265	0.183	132.000	40.630	3.248	-197.050	256.937	-0.766	-41.082
13	BEC 4270	0.077	110.000	31.048	3.542	-114.809	156.568	-0.733	-17.910
14	EC 7	0.049	62.000	8.816	7.032	3.118	73.265	0.042	0.807
15	EC 11	0.018	110.000	28.938	3.801	-76.514	147.204	-0.519	-11.567
16	EC 15	0.049	500.000	58.472	8.551	-182.478	905.657	-0.201	-13.605
17	EC 16	0.592	500.000	65.924	7.584	-973.868	1140.417	-0.853	-58.996
18	EC DAN 3	0.106	107.000	19.593	5.461	-0.290	124.219	-0.002	-0.037
19	EC DAN 5	0.099	98.000	13.235	7.404	-22.510	124.561	-0.180	-4.148
20	GB45/64/7	0.049	66.000	15.595	4.232	1.289	75.507	0.017	0.250
21	GB45/64/10	0.155	66.000	16.284	4.052	-18.487	77.021	-0.240	-3.232
22	GB47/64/8	0.141	34.000	25.900	1.312	20.186	35.800	0.563	6.845
23	GB47/64/10	0.028	36.000	5.845	6.158	-0.105	41.404	-0.002	-0.037
24	GB48/65/5	0.035	73.000	4.267	17.107	0.083	84.204	0.000	0.015
25	GB48/65/9	0.014	97.000	10.886	8.910	0.650	116.316	0.005	0.111
26	GB48/65/12	0.028	75.000	9.389	7.987	5.853	101.703	0.057	2.174
27	SEC 1	0.141	17.000	10.588	1.605	9.565	18.367	0.520	8.743
28	SEC 9	0.028	15.000	7.113	2.108	-5.354	18.421	-0.290	-5.136
29	SEC 13	0.092	14.000	5.173	2.705	-1.010	19.172	-0.052	-1.849
30	SEC 25	0.472	208.000	96.602	2.153	-259.908	257.288	-1.010	-11.908
31	SEC 26	0.204	50.000	32.115	1.556	15.219	53.714	0.283	2.937
32	WEC 5B	0.010	13.000	50.505	0.257	75.256	10.768	6.988	20.029
33	WEC 5C	0.028	20.000	14.941	1.338	9.918	20.578	0.481	2.692
34	LDW3WB	0.010	6.600	36.231	0.182	39.124	2.909	13.446	60.406
35	LDW4WB	0.018	6.700	9.667	0.693	24.670	4.948	4.985	32.697
36	JP 5	0.010	23.000	116.279	0.197	197.625	18.632	10.606	20.965
37	A62/5	0.035	80.000	7.137	11.209	1062.040	-195.695	-5.426	290.999
38	EC 7	0.290	62.000	55.028	1.126	311.390	14.284	21.798	80.660

Table 1
Lithium.

TABLE 2 SODIUM

REF	SAMPLE	X	CW	CF	CWCF	CO	CI	COCI	PER
1	A62/2	1.200	0.070	0.008	8.151	0.000	0.104	0.005	0.294
2	A62/5	3.700	0.080	0.071	1.118	0.068	0.083	0.829	18.880
3	A76/3	1.600	0.000	0.017	0.000	0.020	-0.012	-1.590	0.775
4	A76/5	2.800	0.040	0.036	1.096	0.035	0.041	0.860	17.881
5	A76/6	25.200	0.040	0.183	0.217	0.296	-0.109	-2.714	272.812
6	A78/3	4.000	0.120	0.023	5.171	0.006	0.196	0.033	2.192
7	A78/4	1.200	0.170	0.058	2.884	0.052	0.199	0.261	6.238
8	A78/9	10.400	0.130	0.067	1.933	0.023	0.163	0.145	4.410
9	A78/10	8.000	0.130	0.058	2.211	0.028	0.163	0.174	5.463
10	A78/11	0.900	0.040	0.007	5.598	0.002	0.070	0.037	2.902
11	AEC 1	27.500	0.460	0.168	2.732	-0.305	0.690	-0.442	-15.385
12	BEC 4265	5.900	0.330	0.130	2.519	-0.386	0.602	-0.642	-32.246
13	BEC 4270	2.900	0.820	0.116	7.012	-1.181	1.234	-0.957	-24.733
14	EC 7	1.600	3.060	0.028	106.296	-0.295	3.702	-0.079	-1.553
15	EC 11	0.500	0.680	0.080	8.459	-0.699	0.955	-0.732	-17.110
16	EC 15	0.500	0.680	0.059	11.396	-0.278	1.249	-0.223	-15.288
17	EC 16	7.400	0.130	0.082	1.577	-0.031	0.200	-0.157	-7.363
18	EC DAN 3	4.600	0.700	0.085	8.232	-0.054	0.821	-0.066	-1.084
19	EC DAN 5	7.400	0.250	0.098	2.527	0.035	0.297	0.118	2.544
20	GB45/64/7	3.400	0.680	0.108	6.284	-0.054	0.787	-0.068	-1.018
21	GB45/64/10	14.300	0.700	0.150	4.659	-0.234	0.821	-0.285	-3.862
22	GB47/64/8	14.800	0.650	0.271	2.390	0.005	0.734	0.006	0.090
23	GB47/64/10	10.400	0.470	0.217	2.164	0.167	0.515	0.324	4.632
24	GB48/65/5	3.300	0.560	0.040	13.918	0.008	0.644	0.013	0.204
25	GB48/65/9	0.800	0.630	0.062	10.127	-0.005	0.757	-0.006	-0.140
26	GB48/65/12	1.600	0.130	0.053	2.422	0.049	0.161	0.307	10.616
27	SEC 1	2.800	0.730	0.021	34.716	-0.092	0.881	-0.104	-1.961
28	SEC 9	12.900	0.730	0.327	2.227	-0.308	0.904	-0.340	-6.075
29	SEC 13	15.700	0.390	0.088	4.417	-0.123	0.566	-0.217	-8.089
30	SEC 25	15.300	0.250	0.313	0.798	0.515	0.222	2.320	19.639
31	SEC 26	11.900	0.560	0.187	2.989	-0.164	0.637	-0.258	-2.838
32	WEC 5B	0.500	0.100	0.252	0.395	0.353	0.090	3.884	12.220
33	WEC 5C	3.700	0.150	0.197	0.759	0.244	0.144	1.691	8.852
34	LDW3WB	3.300	0.870	1.195	0.727	1.227	0.829	1.479	14.376
35	LDW4WB	23.600	0.860	1.267	0.678	3.327	0.619	5.371	34.361
36	JP 5	0.250	0.870	0.290	2.992	-0.214	0.897	-0.239	-0.601
37	A62/5	6.900	0.080	0.140	0.568	-0.738	0.309	-2.383	-202.247
38	EC 7	7.400	3.060	0.140	21.792	107.501	-16.922	-6.352	564.206

Table 2
Sodium.

TABLE 3 POTASSIUM

REF	SAMPLE	X	CW	CF	CWCF	CO	CI	COCI	PER
1	A62/2	10.150	0.850	0.072	11.702	-0.028	1.283	-0.021	-1.095
2	A62/5	10.150	0.960	0.196	4.893	-0.038	1.240	-0.030	-0.868
3	A76/3	3.250	0.450	0.035	12.688	-0.027	0.749	-0.036	-2.320
4	A76/5	10.150	1.100	0.132	8.318	-0.156	1.417	-0.110	-2.873
5	A76/6	92.650	0.750	0.675	1.110	0.616	0.827	0.744	30.223
6	A78/3	6.750	0.750	0.039	19.153	-0.083	1.310	-0.063	-4.459
7	A78/4	1.150	1.710	0.056	30.274	-0.042	2.156	-0.019	-0.507
8	A78/9	46.650	1.510	0.301	5.007	-0.533	2.157	-0.247	-8.507
9	A78/10	26.650	0.880	0.195	4.493	-0.094	1.203	-0.078	-2.686
10	A78/11	3.650	0.510	0.028	17.599	-0.037	0.949	-0.039	-3.270
11	AEC 1	210.650	2.220	1.289	1.721	-0.221	2.956	-0.075	-2.315
12	BEC 4265	21.050	1.170	0.467	2.503	-1.360	2.130	-0.638	-31.999
13	BEC 4270	14.150	1.340	0.570	2.348	-0.850	1.793	-0.474	-10.896
14	EC 7	9.750	1.510	0.175	8.607	0.032	1.792	0.018	0.344
15	EC 11	3.250	1.250	0.522	2.392	-0.423	1.583	-0.267	-5.639
16	EC 15	0.400	0.100	0.047	2.094	0.019	0.148	0.129	7.161
17	EC 16	9.750	1.320	0.108	12.157	-2.793	3.107	-0.898	-64.097
18	EC DAN 3	21.450	2.520	0.396	6.355	-0.086	2.938	-0.029	-0.475
19	EC DAN 5	44.450	2.080	0.594	3.500	-0.032	2.545	-0.012	-0.280
20	GB45/64/7	16.050	2.610	0.510	5.109	-0.084	3.005	-0.028	-0.416
21	GB45/64/10	87.650	2.660	0.920	2.888	-0.295	3.045	-0.097	-1.282
22	GB47/64/8	26.650	2.570	0.489	5.249	-0.978	3.032	-0.322	-4.387
23	GB47/64/10	19.050	2.920	0.397	7.342	-0.100	3.372	-0.029	-0.446
24	GB48/65/5	10.150	2.420	0.123	19.555	-0.016	2.794	-0.005	-0.088
25	GB48/65/9	2.780	2.470	0.216	11.425	-0.051	2.975	-0.017	-0.349
26	GB48/65/12	2.400	2.190	0.080	27.210	-0.033	3.048	-0.010	-0.422
27	SEC 1	9.990	2.280	0.075	30.390	-0.276	2.750	-0.100	-1.887
28	SEC 9	63.650	2.720	1.617	1.681	-0.126	3.198	-0.039	-0.669
29	SEC 13	145.650	2.160	0.819	2.637	-0.120	2.945	-0.040	-1.428
30	SEC 25	32.450	1.440	0.664	2.168	-1.818	1.783	-1.019	-12.037
31	SEC 26	90.650	2.840	1.427	1.990	0.092	3.133	0.029	0.313
32	WEC 5B	3.650	3.450	1.843	1.871	0.783	3.545	0.220	0.785
33	WEC 5C	26.650	2.940	1.422	2.067	-0.085	3.113	-0.027	-0.157
34	LDW3WB	4.250	2.870	1.539	1.863	1.410	3.035	0.464	5.006
35	LDW4WB	45.450	3.030	2.440	1.241	-0.537	3.377	-0.159	-1.576
36	JP 5	0.150	0.340	0.174	1.949	0.030	0.347	0.086	0.215
37	A62/5	44.450	0.960	0.906	1.059	1.682	0.757	2.221	38.414
38	EC 7	72.650	1.510	1.378	1.095	6.212	0.610	10.177	66.069

Table 3
Potassium.

TABLE 4 RUBIDIUM

REF	SAMPLE	X	CW	CF	CWCF	CO	CI	COCI	PER
1	A62/2	0.300	67.000	21.468	3.120	15.563	92.403	0.168	7.679
2	A62/5	0.100	62.000	19.327	3.207	6.243	77.653	0.080	2.207
3	A76/3	0.100	35.000	10.912	3.207	7.279	52.426	0.138	8.028
4	A76/5	0.100	76.000	13.027	5.833	-5.764	96.684	-0.059	-1.531
5	A76/6	2.800	51.000	204.081	0.249	324.591	-108.101	-3.002	234.024
6	A78/3	0.100	34.000	5.801	5.860	0.947	56.219	0.016	1.120
7	A78/4	0.100	90.000	49.115	1.832	46.661	101.031	0.461	10.519
8	A78/9	2.100	109.000	135.746	0.802	154.237	94.667	1.629	34.045
9	A78/10	1.400	59.000	102.880	0.573	121.530	38.267	3.175	51.289
10	A78/11	0.100	26.000	7.939	3.274	5.444	42.501	0.128	9.324
11	AEC 1	6.310	-	386.310	-	-	-	-	-
12	BEC 4265	0.600	-	133.214	-	-	-	-	-
13	BEC 4270	0.600	-	241.935	-	-	-	-	-
14	EC 7	0.100	109.000	17.992	6.058	8.241	128.277	0.064	1.214
15	EC 11	0.750	107.000	1205.788	0.088	2635.209	-397.307	-6.632	409.565
16	EC 15	0.100	4.400	119.331	0.036	182.052	-101.194	-1.799	1542.481
17	EC 16	0.300	12.000	33.407	0.359	84.687	-19.583	-4.324	213.765
18	EC DAN 3	0.600	165.000	110.905	1.487	98.600	175.656	0.561	8.264
19	EC DAN 5	1.600	159.000	213.903	0.743	237.056	141.795	1.671	26.926
20	GB45/64/7	1.130	161.000	359.643	0.447	416.020	123.532	3.367	33.100
21	GB45/64/10	2.600	169.000	273.166	0.618	346.024	145.906	2.371	23.627
22	GB47/64/8	0.880	160.000	161.645	0.989	162.806	159.634	1.019	11.732
23	GB47/64/10	0.660	154.000	137.787	1.117	134.587	156.905	0.857	11.378
24	GB48/65/5	0.600	166.000	73.152	2.269	67.501	181.136	0.372	5.416
25	GB48/65/9	0.100	180.000	77.760	2.314	65.607	202.933	0.323	6.086
26	GB48/65/12	0.100	137.000	33.534	4.085	27.958	179.111	0.156	5.685
27	SEC 1	0.100	148.000	7.509	19.707	-14.913	177.974	-0.083	-1.565
28	SEC 9	1.810	180.000	459.857	0.391	902.306	58.589	15.400	72.134
29	SEC 13	4.600	159.000	258.688	0.614	328.534	100.573	3.266	52.958
30	SEC 25	1.130	52.000	231.273	0.224	805.009	-27.321	-29.464	147.533
31	SEC 26	2.750	202.000	432.934	0.466	651.112	154.031	4.227	31.105
32	WEC 5B	0.100	-	505.050	-	-	-	-	-
33	WEC 5C	0.750	-	400.213	-	-	-	-	-
34	LDW3WB	0.100	-	362.318	-	-	-	-	-
35	LDW4WB	1.220	-	655.209	-	-	-	-	-
36	JP 5	0.300	23.000	3488.372	0.006	6510.430	-139.252	-46.752	690.671
37	A62/5	1.400	62.000	285.481	0.217	-2950.060	907.598	-3.250	-1042.988
38	EC 7	2.420	109.000	459.203	0.237	*********	2505.891	-4.955	-1829.765

Table 4
Rubidium.

TABLE 5 CAESIUM

REF	SAMPLE	X	CW	CF	CWCF	CO	CI	CDCI	PER
1	A62/2	0.075	6.600	5.367	1.229	5.207	7.287	0.714	26.083
2	A62/5	0.150	6.600	28.991	0.227	35.856	-1.613	-22.223	119.087
3	A76/3	0.075	3.500	8.184	0.427	8.890	0.111	80.029	98.051
4	A76/5	0.075	5.800	9.770	0.593	10.955	4.495	2.436	38.136
5	A76/6	0.150	4.000	10.932	0.365	16.390	-3.205	-5.113	150.671
6	A78/3	0.150	3.000	8.701	0.344	9.683	-1.492	-6.487	129.753
7	A78/4	0.075	4.900	36.836	0.133	38.754	-3.717	-10.424	160.475
8	A78/9	0.075	8.500	4.848	1.753	2.323	10.456	0.222	6.576
9	A78/10	0.075	5.600	5.511	1.016	5.473	5.641	0.970	24.339
10	A78/11	0.075	2.700	5.954	0.453	6.403	-0.273	-23.434	105.613
11	AEC 1	0.150	17.000	9.183	1.851	-3.516	23.187	-0.151	-4.792
12	BEC 4265	0.075	7.200	16.651	0.432	41.239	-5.724	-7.204	157.625
13	BEC 4270	0.075	9.800	30.241	0.324	68.006	-2.257	-30.126	119.081
14	EC 7	0.075	5.500	13.494	0.407	14.350	3.806	3.769	41.903
15	EC 11	0.075	8.800	120.578	0.072	265.992	-42.502	-6.258	502.665
16	EC 15	0.075	-	89.498	-	-	-	-	-
17	EC 16	0.075	-	8.351	-	-	-	-	-
18	EC DAN 3	0.075	7.700	13.863	0.555	15.265	6.485	2.353	27.417
19	EC DAN 5	0.075	10.000	10.026	0.997	10.038	9.991	1.004	18.128
20	GB45/64/7	0.075	6.500	23.870	0.272	28.799	3.223	8.933	56.758
21	GB45/64/10	0.075	8.500	7.879	1.078	7.446	8.637	0.862	10.109
22	GB47/64/8	0.150	6.000	27.553	0.217	42.756	1.209	35.346	82.163
23	GB47/64/10	0.075	5.600	15.657	0.357	17.642	3.797	4.645	41.018
24	GB48/65/5	0.075	8.300	9.144	0.907	9.195	8.162	1.126	14.757
25	GB48/65/9	0.075	10.500	58.320	0.180	64.004	-0.226	-282.438	101.797
26	GB48/65/12	0.075	3.600	25.150	0.143	26.312	-5.171	-5.088	203.628
27	SEC 1	0.075	9.900	5.632	1.757	4.951	10.810	0.457	7.771
28	SEC 9	0.075	11.000	19.054	0.577	31.789	7.505	4.235	41.586
29	SEC 13	0.075	12.000	4.217	2.845	-1.234	16.561	-0.074	-2.637
30	SEC 25	0.075	8.700	15.349	0.566	36.632	5.757	6.362	40.127
31	SEC 26	0.075	16.000	11.807	1.355	7.846	16.870	0.465	4.732
32	WEC 5B	0.075	7.200	378.787	0.019	624.015	-14.906	-41.861	299.874
33	WEC 5C	0.075	5.800	40.021	0.144	74.002	1.883	39.280	69.281
34	LOW3WB	0.075	7.700	271.739	0.028	297.515	-25.182	-11.814	393.725
35	LOW4WB	0.075	10.000	40.279	0.248	193.392	-7.872	-24.566	171.732
36	JP 5	0.075	5.800	872.093	0.006	1627.564	-34.760	-46.821	684.699
37	A62/5	0.075	6.600	15.293	0.431	-110.572	39.494	-2.799	-367.233
38	EC 7	0.075	5.500	14.231	0.386	-306.849	65.260	-4.701	-895.999

Table 5
Caesium

TABLE 6 MAGNESIUM

REF	SAMPLE	X	CW	CF	CWCF	CO	CI	COCI	PER
1	A62/2	4.440	0.360	0.031	11.330	-0.010	0.543	-0.019	-0.991
2	A62/5	2.340	0.350	0.045	7.738	-0.048	0.461	-0.104	-3.020
3	A76/3	1.490	0.290	0.016	17.835	-0.025	0.488	-0.051	-3.330
4	A76/5	4.130	0.370	0.053	6.876	-0.040	0.473	-0.085	-2.212
5	A76/6	9.220	0.280	0.067	4.166	-0.100	0.501	-0.200	-13.174
6	A78/3	2.630	0.150	0.015	9.831	-0.007	0.256	-0.030	-2.126
7	A78/4	0.270	0.290	0.013	21.868	-0.003	0.364	-0.009	-0.234
8	A78/9	7.060	0.410	0.045	8.983	-0.206	0.605	-0.340	-12.104
9	A78/10	3.370	0.190	0.024	7.672	-0.045	0.268	-0.169	-5.957
10	A78/11	6.380	0.280	0.050	5.528	0.018	0.489	0.038	3.017
11	AEC 1	15.070	0.550	0.092	5.961	-0.651	0.912	-0.714	-27.441
12	BEC 4265	10.390	0.520	0.230	2.254	-0.521	0.915	-0.570	-27.621
13	BEC 4270	6.890	0.790	0.277	2.843	-0.668	1.092	-0.612	-14.518
14	EC 7	3.520	0.660	0.063	10.421	-0.000	0.786	-0.000	-0.014
15	EC 11	0.940	0.830	0.151	5.492	-0.732	1.141	-0.641	-14.667
16	EC 15	0.670	0.140	0.079	1.751	0.047	0.195	0.241	12.564
17	EC 16	2.630	0.320	0.029	10.926	-0.667	0.748	-0.890	-63.144
18	EC DAN 3	6.050	1.120	0.111	10.015	-0.117	1.318	-0.089	-1.451
19	EC DAN 5	9.980	0.680	0.133	5.096	-0.097	0.851	-0.114	-2.578
20	GB45/64/7	3.670	0.950	0.116	8.133	-0.119	1.107	-0.108	-1.613
21	GB45/64/10	12.610	1.230	0.132	9.284	-0.635	1.473	-0.431	-5.959
22	GB47/64/8	8.480	0.960	0.155	6.163	-0.411	1.138	-0.361	-4.942
23	GB47/64/10	1.630	0.570	0.034	16.750	-0.071	0.666	-0.107	-1.638
24	GB48/65/5	4.750	1.030	0.057	17.785	-0.001	1.188	-0.001	-0.016
25	GB48/65/9	0.810	0.950	0.062	15.082	-0.042	1.148	-0.036	-0.746
26	GB48/65/12	0.400	0.360	0.013	26.837	-0.005	0.501	-0.010	-0.407
27	SEC 1	2.630	0.520	0.019	26.328	-0.060	0.626	-0.095	-1.795
28	SEC 9	9.600	0.660	0.243	2.706	-0.413	0.840	-0.492	-9.025
29	SEC 13	8.840	0.430	0.049	8.649	-0.216	0.652	-0.331	-12.918
30	SEC 25	38.960	2.190	0.797	2.746	-3.659	2.806	-1.304	-15.924
31	SEC 26	19.110	1.240	0.300	4.121	-0.586	1.435	-0.408	-4.563
32	WEC 5B	0.670	0.600	0.338	1.773	0.165	0.615	0.269	0.955
33	WEC 5C	3.520	0.370	0.187	1.969	0.006	0.390	0.017	0.101
34	LDW3WB	0.670	0.570	0.242	2.348	0.210	0.610	0.345	3.768
35	LDW4WB	4.750	0.620	0.255	2.430	-1.590	0.835	-1.903	-22.773
36	JP 5	1.490	2.300	1.732	1.327	1.237	2.326	0.531	1.313
37	A62/5	3.970	0.350	0.080	4.323	3.976	-0.668	-5.952	249.022
38	EC 7	15.070	0.660	0.285	2.308	14.040	-1.900	-7.389	341.651

Table 6
Magnesium

TABLE 7 CALCIUM

REF	SAMPLE	X	CW	CF	CWCF	CO	CI	COCI	PER
1	A62/2	17.850	0.200	0.127	1.565	0.118	0.240	0.492	19.565
2	A62/5	7.199	0.090	0.139	0.646	0.154	0.071	2.143	37.563
3	A76/3	10.050	0.510	0.109	4.650	0.049	0.799	0.061	3.730
4	A76/5	10.050	0.140	0.130	1.069	0.128	0.142	0.896	18.491
5	A76/6	8.850	0.120	0.064	1.860	0.020	0.177	0.117	6.378
6	A78/3	13.649	0.080	0.079	1.010	0.079	0.080	0.980	39.720
7	A78/4	2.099	0.060	0.103	0.581	0.105	0.048	2.186	35.755
8	A78/9	9.750	0.090	0.063	1.427	0.044	0.104	0.424	11.863
9	A78/10	9.149	0.110	0.067	1.635	0.049	0.130	0.376	11.106
10	A78/11	23.400	0.690	0.185	3.714	0.116	1.150	0.100	7.494
11	AEC 1	4.650	0.120	0.028	4.215	-0.120	0.192	-0.624	-23.215
12	BEC 4265	5.400	0.170	0.119	1.417	-0.010	0.238	-0.043	-1.691
13	BEC 4270	8.100	0.410	0.326	1.255	0.172	0.459	0.375	7.222
14	EC 7	2.700	0.220	0.048	4.528	0.030	0.256	0.117	2.205
15	EC 11	0.600	0.460	0.096	4.768	-0.376	0.626	-0.600	-13.610
16	EC 15	5.850	0.410	0.698	0.587	0.855	0.145	5.885	77.770
17	EC 16	6.600	0.060	0.073	0.816	0.105	0.040	2.639	53.424
18	EC DAN 3	7.500	0.580	0.138	4.183	0.038	0.666	0.057	0.911
19	EC DAN 5	18.450	0.240	0.246	0.973	0.249	0.237	1.048	18.772
20	GB45/64/7	2.250	0.370	0.071	5.166	-0.013	0.426	-0.030	-0.452
21	GB45/64/10	19.049	0.960	0.200	4.796	-0.331	1.128	-0.293	-3.982
22	GB47/64/8	9.899	1.380	0.181	7.588	-0.663	1.646	-0.402	-5.541
23	GB47/64/10	2.400	0.170	0.050	3.392	0.026	0.191	0.138	2.025
24	GB48/65/5	22.200	1.970	0.270	7.278	0.167	2.247	0.074	1.130
25	GB48/65/9	0.150	0.240	0.011	20.576	-0.015	0.291	-0.053	-1.076
26	GB48/65/12	1.650	0.100	0.055	1.807	0.052	0.118	0.447	14.744
27	SEC 1	15.149	0.370	0.113	3.252	0.072	0.424	0.171	3.060
28	SEC 9	2.099	0.240	0.053	4.498	-0.241	0.320	-0.753	-14.493
29	SEC 13	2.700	0.100	0.015	6.585	-0.044	0.149	-0.295	-11.339
30	SEC 25	3.599	0.560	0.073	7.600	-1.482	0.775	-1.912	-25.232
31	SEC 26	3.000	0.190	0.047	4.022	-0.087	0.219	-0.399	-4.451
32	WEC 5B	14.100	9.260	7.121	1.300	5.709	9.387	0.608	2.133
33	WEC 5C	5.250	0.110	0.280	0.392	0.449	0.090	4.960	22.169
34	LDW3WB	0.150	0.160	0.054	2.944	0.044	0.173	0.254	2.804
35	LDW4WB	2.400	0.160	0.128	1.241	-0.028	0.178	-0.159	-1.576
36	JP 5	0.300	1.170	0.348	3.354	-0.367	1.208	-0.303	-0.765
37	A62/5	1.350	0.090	0.027	3.269	0.931	-0.146	-6.367	226.990
38	EC 7	7.500	0.220	0.142	1.545	2.999	-0.311	-9.621	218.927

Table 7
Calcium.

TABLE 8 STRONTIUM

REF	SAMPLE	X	CW	CF	CWCF	CO	CI	COCI	PER
1	A62/2	2.594	288.000	185.701	1.550	172.435	345.074	0.499	19.794
2	A62/5	0.360	113.000	69.578	1.624	56.264	128.927	0.436	10.914
3	A76/3	1.950	883.000	212.789	4.149	111.710	1367.882	0.081	4.883
4	A76/5	0.914	167.000	119.202	1.400	104.939	182.699	0.574	12.686
5	A76/6	0.330	145.000	24.052	6.028	-71.160	270.703	-0.262	-18.045
6	A78/3	1.049	88.000	60.911	1.444	56.249	109.343	0.514	25.695
7	A78/4	0.060	110.000	29.469	3.732	24.634	131.729	0.187	4.543
8	A78/9	0.840	137.000	54.298	2.523	-2.876	181.316	-0.015	-0.505
9	A78/10	0.780	125.000	57.319	2.180	28.554	156.977	0.181	5.687
10	A78/11	0.585	138.000	46.443	2.971	33.798	221.650	0.152	10.906
11	AEC 1	0.390	108.000	23.876	4.523	-112.793	174.585	-0.646	-24.198
12	BEC 4265	0.240	94.000	53.285	1.764	-52.624	149.671	-0.351	-15.406
13	BEC 4270	0.269	179.000	108.870	1.644	-20.687	220.364	-0.093	-1.983
14	EC 7	0.524	222.000	94.458	2.350	80.793	249.016	0.324	5.844
15	EC 11	0.015	96.000	24.115	3.980	-69.398	128.992	-0.538	-12.021
16	EC 15	0.090	48.000	107.398	0.446	139.813	-6.572	-21.271	108.588
17	EC 16	0.120	107.000	13.363	8.007	-210.936	245.148	-0.860	-59.712
18	EC DAN 3	0.090	177.000	16.635	10.639	-19.844	208.592	-0.095	-1.550
19	EC DAN 5	0.210	130.000	28.074	4.630	-14.907	161.938	-0.092	-2.070
20	GB45/64/7	0.030	185.000	9.548	19.375	-40.246	218.093	-0.184	-2.786
21	GB45/64/10	0.750	223.000	78.798	2.830	-22.060	254.969	-0.086	-1.141
22	GB47/64/8	0.120	201.000	22.042	9.118	-104.190	240.774	-0.432	-5.976
23	GB47/64/10	0.015	193.000	3.131	61.631	-34.336	227.029	-0.151	-2.316
24	GB48/65/5	0.210	224.000	25.603	8.748	13.527	256.343	0.052	0.804
25	GB48/65/9	0.030	159.000	23.328	6.815	7.201	189.432	0.038	0.756
26	GB48/65/12	0.060	110.000	20.120	5.467	15.276	146.581	0.104	3.869
27	SEC 1	1.005	187.000	75.473	2.477	57.672	210.795	0.273	4.792
28	SEC 9	0.210	259.000	53.353	4.854	-271.768	348.215	-0.780	-15.099
29	SEC 13	0.300	100.000	16.870	5.927	-41.372	148.721	-0.278	-10.603
30	SEC 25	0.090	121.000	18.419	6.568	-309.872	166.387	-1.862	-24.405
31	SEC 26	0.090	121.000	14.168	8.539	-86.760	143.190	-0.605	-6.919
32	WEC 5B	0.015	406.000	75.757	5.359	-142.183	425.647	-0.334	-1.211
33	WEC 5C	0.180	579.000	96.051	6.028	-383.510	634.265	-0.604	-3.596
34	LDW3WB	0.015	243.000	54.347	4.471	35.931	266.494	0.134	1.506
35	LDW4WB	0.780	674.000	418.904	1.608	-871.034	824.569	-1.056	-11.475
36	JP 5	0.015	205.000	174.418	1.175	147.749	206.431	0.715	1.758
37	A62/5	0.120	113.000	24.469	4.617	1306.202	-221.976	-5.884	253.380
38	EC 7	0.420	222.000	79.696	2.785	5312.586	-751.967	-7.064	384.324

Table 8
Strontium

TABLE 9 CHROMIUM

REF	SAMPLE	X	CW	CF	CWCF	CO	CI	COCI	PER
1	A62/2	0.777	137.000	55.603	2.463	45.047	182.413	0.246	10.870
2	A62/5	1.124	294.000	217.240	1.353	193.703	322.156	0.601	14.442
3	A76/3	0.612	162.000	66.783	2.425	52.422	230.887	0.227	12.490
4	A76/5	1.240	225.000	161.542	1.392	142.605	245.843	0.580	12.796
5	A76/6	0.529	120.000	38.556	3.112	-25.557	204.645	-0.124	-7.831
6	A78/3	3.454	418.000	200.371	2.086	162.912	589.480	0.276	15.667
7	A78/4	0.430	230.000	211.198	1.089	210.069	235.073	0.893	18.531
8	A78/9	1.356	135.000	87.653	1.540	54.920	160.371	0.342	9.788
9	A78/10	1.405	118.000	103.248	1.142	96.978	124.969	0.776	20.464
10	A78/11	1.075	187.000	85.344	2.191	71.304	279.877	0.254	16.979
11	AEC 1	0.661	-	40.467	-	-	-	-	-
12	BEC 4265	0.893	-	198.268	-	-	-	-	-
13	BEC 4270	0.232	-	93.548	-	-	-	-	-
14	EC 7	0.496	103.000	89.240	1.154	87.766	105.914	0.828	13.684
15	EC 11	0.017	290.000	27.331	10.610	-314.376	410.556	-0.765	-18.027
16	EC 15	0.017	185.000	20.286	9.119	-69.601	336.332	-0.206	-14.025
17	EC 16	1.842	255.000	205.122	1.243	85.644	328.587	0.260	10.173
18	EC DAN 3	0.298	99.000	55.083	1.797	45.092	107.651	0.418	6.299
19	EC DAN 5	0.628	113.000	83.957	1.345	71.709	122.100	0.587	11.460
20	GB45/64/7	0.199	117.000	63.335	1.847	48.104	127.122	0.378	5.266
21	GB45/64/10	1.141	113.000	119.878	0.942	124.689	111.475	1.118	12.733
22	GB47/64/8	0.777	119.000	142.725	0.833	159.461	113.726	1.402	15.450
23	GB47/64/10	0.909	186.000	189.770	0.980	190.514	185.324	1.028	13.336
24	GB48/65/5	0.281	111.000	34.259	3.239	29.588	123.510	0.239	3.550
25	GB48/65/9	0.010	125.000	7.776	16.075	-6.157	151.294	-0.040	-0.822
26	GB48/65/12	0.364	119.000	122.065	0.974	122.231	117.752	1.038	28.616
27	SEC 1	1.042	48.000	78.251	0.613	83.080	41.545	1.999	26.897
28	SEC 9	0.166	57.000	42.174	1.351	18.736	63.431	0.295	4.730
29	SEC 13	0.645	39.000	36.272	1.075	34.361	40.598	0.846	22.581
30	SEC 25	0.331	57.000	67.744	0.841	102.130	52.245	1.954	17.075
31	SEC 26	0.579	104.000	91.152	1.140	79.014	106.668	0.740	7.331
32	WEC 5B	0.010	-	50.505	-	-	-	-	-
33	WEC 5C	0.099	-	52.828	-	-	-	-	-
34	LDW3WB	0.010	-	36.231	-	-	-	-	-
35	LDW4WB	0.132	-	70.891	-	-	-	-	-
36	JP 5	0.010	530.000	116.279	4.557	-244.515	549.370	-0.445	-1.125
37	A62/S	1.455	294.000	296.696	0.990	257.656	304.203	0.846	19.210
38	EC 7	0.827	103.000	156.925	0.656	-1826.078	472.085	-3.868	-284.726

Table 9
Chromium.

TABLE 10 MOLYBDENUM

REF	SAMPLE	X	CW	CF	CWCF	CO	CI	COCI	PER
1	A62/2	0.500	-	35.780	-	-	-	-	-
2	A62/5	0.500	-	96.637	-	-	-	-	-
3	A76/3	0.500	-	54.561	-	-	-	-	-
4	A76/5	0.500	-	65.138	-	-	-	-	-
5	A76/6	0.500	-	36.443	-	-	-	-	-
6	A78/3	0.500	-	29.005	-	-	-	-	-
7	A78/4	0.500	-	245.579	-	-	-	-	-
8	A78/9	0.500	-	32.320	-	-	-	-	-
9	A78/10	0.500	-	36.743	-	-	-	-	-
10	A78/11	0.500	-	39.695	-	-	-	-	-
11	AEC 1	0.500	-	30.610	-	-	-	-	-
12	BEC 4265	0.500	-	111.012	-	-	-	-	-
13	BEC 4270	0.500	-	201.612	-	-	-	-	-
14	EC 7	0.500	-	89.960	-	-	-	-	-
15	EC 11	0.500	-	803.858	-	-	-	-	-
16	EC 15	0.500	-	596.658	-	-	-	-	-
17	EC 16	0.500	-	55.679	-	-	-	-	-
18	EC DAN 3	0.500	-	92.421	-	-	-	-	-
19	EC DAN 5	0.500	-	66.844	-	-	-	-	-
20	GB45/64/7	0.500	-	159.134	-	-	-	-	-
21	GB45/64/10	0.500	-	52.532	-	-	-	-	-
22	GB47/64/8	0.500	-	91.844	-	-	-	-	-
23	GB47/64/10	0.500	-	104.384	-	-	-	-	-
24	GB48/65/5	0.500	-	60.960	-	-	-	-	-
25	GB48/65/9	0.500	-	388.802	-	-	-	-	-
26	GB48/65/12	0.500	-	167.672	-	-	-	-	-
27	SEC 1	0.500	-	37.548	-	-	-	-	-
28	SEC 9	0.500	-	127.032	-	-	-	-	-
29	SEC 13	0.500	-	28.118	-	-	-	-	-
30	SEC 25	0.500	-	102.333	-	-	-	-	-
31	SEC 26	0.500	-	78.715	-	-	-	-	-
32	WEC 5B	0.500	-	2525.252	-	-	-	-	-
33	WEC 5C	0.500	-	266.809	-	-	-	-	-
34	LDW3WB	0.500	-	1811.594	-	-	-	-	-
35	LDW4WB	0.500	-	268.528	-	-	-	-	-
36	JP 5	0.500	-	5813.955	-	-	-	-	-
37	A62/5	0.500	-	101.957	-	-	-	-	-
38	EC 7	0.500	-	94.876	-	-	-	-	-

Table 10
Molybdenum

TABLE 11 MANGANESE

REF	SAMPLE	X	CW	CF	CWCF	CO	CI	COCI	PER
1	A62/2	0.660	0.040	0.004	8.469	0.000	0.059	0.002	0.122
2	A62/5	0.070	0.010	0.001	7.391	-0.001	0.013	-0.098	-2.846
3	A76/3	0.030	0.010	0.000	30.546	-0.001	0.016	-0.066	-4.367
4	A76/5	1.690	0.050	0.022	2.271	0.013	0.059	0.230	5.518
5	A76/6	0.860	0.010	0.006	1.595	0.003	0.013	0.239	12.246
6	A78/3	0.260	0.010	0.001	6.630	0.000	0.016	0.002	0.187
7	A78/4	0.030	0.010	0.001	6.786	0.000	0.012	0.078	1.950
8	A78/9	0.230	0.010	0.001	6.726	-0.004	0.014	-0.302	-10.583
9	A78/10	0.390	0.010	0.002	3.489	-0.000	0.013	-0.012	-0.413
10	A78/11	0.030	0.010	0.000	41.986	-0.001	0.018	-0.058	-4.942
11	AEC 1	0.180	0.010	0.001	9.074	-0.013	0.017	-0.783	-30.941
12	BEC 4265	5.520	0.080	0.122	0.652	0.233	0.021	10.696	80.242
13	BEC 4270	0.590	0.030	0.023	1.261	0.012	0.033	0.365	7.046
14	EC 7	0.180	0.090	0.003	27.790	-0.006	0.108	-0.055	-1.080
15	EC 11	0.180	0.050	0.028	1.727	0.001	0.059	0.025	0.512
16	EC 15	0.030	0.000	0.003	0.000	0.005	-0.003	-1.682	0.206
17	EC 16	0.360	0.010	0.004	2.494	-0.010	0.018	-0.548	-31.326
18	EC DAN 3	0.300	0.040	0.005	7.213	-0.002	0.046	-0.049	-0.792
19	EC DAN 5	1.040	0.060	0.013	4.315	-0.005	0.074	-0.074	-1.666
20	GB45/64/7	0.140	0.050	0.004	11.221	-0.008	0.058	-0.144	-2.170
21	GB45/64/10	1.030	0.050	0.010	4.620	-0.016	0.058	-0.282	-3.826
22	GB47/64/8	1.040	0.060	0.019	3.140	-0.009	0.069	-0.141	-1.872
23	GB47/64/10	0.030	0.020	0.000	31.933	-0.003	0.023	-0.136	-2.081
24	GB48/65/5	0.300	0.050	0.003	13.670	0.000	0.057	0.014	0.222
25	GB48/65/9	0.030	0.030	0.002	12.860	-0.000	0.036	-0.026	-0.532
26	GB48/65/12	0.030	0.010	0.001	9.940	0.000	0.013	0.038	1.452
27	SEC 1	0.340	0.020	0.002	7.832	-0.000	0.023	-0.009	-0.179
28	SEC 9	1.030	0.080	0.026	3.057	-0.058	0.103	-0.570	-10.601
29	SEC 13	0.120	0.000	0.000	0.000	0.001	-0.000	-2.901	0.029
30	SEC 25	8.790	0.170	0.179	0.944	0.211	0.165	1.277	11.861
31	SEC 26	5.330	0.010	0.083	0.119	0.153	-0.005	-28.724	148.357
32	WEC 5B	0.030	0.010	0.015	0.660	0.018	0.009	1.913	6.418
33	WEC 5C	0.230	0.010	0.012	0.814	0.014	0.009	1.491	7.890
34	LDW3WB	0.030	0.000	0.010	0.000	0.011	-0.001	-8.813	0.121
35	LDW4WB	0.030	0.000	0.001	0.000	0.009	-0.000	-10.261	0.086
36	JP 5	0.030	0.110	0.034	3.153	-0.030	0.113	-0.269	-0.679
37	A62/5	0.260	0.010	0.005	1.886	0.073	-0.007	-9.428	160.721
38	EC 7	7.610	0.090	0.144	0.623	-1.856	0.462	-4.014	-331.213

Table 11
Manganese

TABLE 12 IRON

REF	SAMPLE	X	CW	CF	CWCF	CO	CI	COCI	PER
1	A62/2	26.000	1.790	0.186	9.620	-0.021	2.684	-0.008	-0.405
2	A62/5	21.000	1.180	0.405	2.907	0.168	1.463	0.115	3.130
3	A76/3	7.500	1.120	0.081	13.684	-0.074	1.871	-0.039	-2.575
4	A76/5	91.500	3.160	1.192	2.650	0.604	3.806	0.158	3.863
5	A76/6	73.000	1.140	0.532	2.142	0.053	1.771	0.030	1.725
6	A78/3	29.000	0.850	0.168	5.052	0.050	1.387	0.036	2.406
7	A78/4	1.500	1.120	0.073	15.202	0.010	1.402	0.007	0.196
8	A78/9	54.500	1.410	0.352	4.002	-0.378	1.976	-0.191	-6.466
9	A78/10	24.000	0.450	0.176	2.551	0.060	0.579	0.103	3.323
10	A78/11	34.000	1.640	0.269	6.075	0.080	2.891	0.027	2.191
11	AEC 1	87.000	1.110	0.532	2.083	-0.405	1.567	-0.258	-8.461
12	BEC 4265	471.000	7.320	10.457	0.699	18.618	3.029	6.144	69.998
13	BEC 4270	68.000	3.780	2.741	1.378	0.824	4.392	0.187	3.741
14	EC 7	26.000	0.680	0.467	1.453	0.445	0.724	0.613	10.511
15	EC 11	89.500	5.880	14.389	0.408	25.458	1.974	12.892	72.002
16	EC 15	3.000	0.410	0.357	1.145	0.329	0.457	0.720	29.970
17	EC 16	70.000	1.050	0.779	1.347	0.131	1.449	0.090	3.795
18	EC DAN 3	46.000	4.300	0.850	5.057	0.065	4.979	0.013	0.210
19	EC DAN 5	99.000	8.090	1.323	6.112	-1.529	10.210	-0.149	-3.415
20	GB45/64/7	33.000	5.290	1.050	5.036	-0.152	6.089	-0.025	-0.370
21	GB45/64/10	139.000	4.650	1.460	3.184	-0.770	5.357	-0.143	-1.912
22	GB47/64/8	135.000	5.550	2.479	2.238	0.314	6.232	0.050	0.652
23	GB47/64/10	11.000	2.280	0.229	9.928	-0.174	2.647	-0.066	-0.999
24	GB48/65/5	24.000	4.530	0.292	15.481	0.034	5.220	0.006	0.101
25	GB48/65/9	6.000	5.080	0.466	10.888	-0.081	6.114	-0.013	-0.268
26	GB48/65/12	3.000	1.390	0.100	13.816	0.031	1.914	0.016	0.623
27	SEC 1	24.000	1.570	0.180	8.710	-0.041	1.866	-0.022	-0.411
28	SEC 9	59.000	3.320	1.498	2.214	-1.379	4.110	-0.335	-5.981
29	SEC 13	68.000	1.340	0.382	3.504	-0.288	1.901	-0.151	-5.518
30	SEC 25	609.000	26.200	12.464	2.102	-31.495	32.277	-0.975	-11.456
31	SEC 26	214.000	7.110	3.369	2.110	-0.165	7.887	-0.020	-0.224
32	WEC 5B	0.500	0.800	0.252	3.167	-0.108	0.832	-0.130	-0.470
33	WEC 5C	21.500	0.780	1.147	0.679	1.511	0.737	2.048	10.525
34	LDW3WB	2.500	0.810	0.905	0.894	0.915	0.798	1.146	11.512
35	LDW4WB	23.000	1.400	1.235	1.133	0.402	1.497	0.268	2.550
36	JP 5	16.000	20.350	18.604	1.093	17.082	20.431	0.836	2.048
37	A62/5	49.500	1.180	1.009	1.169	3.479	0.534	6.511	64.637
38	EC 7	401.000	0.680	7.609	0.089	-247.193	48.104	-5.138	-5838.118

Table 12
Iron.

TABLE 13 COBALT

REF	SAMPLE	X	CW	CF	CWCF	CO	CI	COCI	PER
1	A62/2	0.112	14.000	8.014	1.746	7.238	17.339	0.417	17.093
2	A62/5	0.476	71.000	91.998	0.771	98.437	63.297	1.555	30.390
3	A76/3	0.204	27.000	22.261	1.212	21.546	30.428	0.708	30.803
4	A76/5	0.128	20.000	16.675	1.199	15.683	21.092	0.743	15.832
5	A76/6	0.262	8.200	19.096	0.429	27.673	-3.124	-8.856	124.094
6	A78/3	0.312	11.000	18.099	0.607	19.321	5.405	3.574	70.611
7	A78/4	0.180	55.000	88.408	0.622	90.414	45.985	1.966	33.354
8	A78/9	0.328	11.000	21.202	0.518	28.255	5.532	5.106	61.802
9	A78/10	0.298	7.500	21.898	0.342	28.018	0.696	40.204	93.021
10	A78/11	0.148	8.600	11.749	0.731	12.184	5.722	2.129	63.091
11	AEC 1	0.320	-	19.591	-	-	-	-	-
12	BEC 4265	0.312	-	69.271	-	-	-	-	-
13	BEC 4270	0.060	-	24.193	-	-	-	-	-
14	EC 7	0.330	23.000	59.373	0.387	63.270	15.295	4.136	44.179
15	EC 11	0.032	14.000	51.446	0.272	100.161	-3.186	-31.429	118.978
16	EC 15	0.020	3.000	23.866	0.125	35.253	-16.171	-2.180	438.084
17	EC 16	0.248	3.000	27.616	0.108	86.584	-33.318	-2.598	874.217
18	EC DAN 3	0.092	13.000	17.005	0.764	17.916	12.210	1.467	19.060
19	EC DAN 5	0.172	18.000	22.994	0.782	25.100	16.434	1.527	25.184
20	GB45/64/7	0.112	18.000	35.646	0.504	40.654	14.671	2.770	28.932
21	GB45/64/10	0.372	16.000	39.083	0.409	55.229	10.882	5.075	39.834
22	GB47/64/8	0.196	14.000	36.002	0.388	51.523	9.109	5.655	42.433
23	GB47/64/10	0.076	15.000	15.866	0.945	16.037	14.844	1.080	13.920
24	GB48/65/5	0.306	33.000	37.307	0.884	37.570	32.297	1.163	15.164
25	GB48/65/9	0.020	33.000	15.552	2.121	13.478	36.913	0.365	6.820
26	GB48/65/12	0.020	9.700	6.706	1.446	6.545	10.918	0.599	18.800
27	SEC 1	0.180	5.600	13.517	0.414	14.781	3.910	3.779	41.018
28	SEC 9	0.060	11.000	15.243	0.721	21.953	9.158	2.396	28.719
29	SEC 13	0.348	5.600	19.570	0.286	29.358	-2.587	-11.344	134.367
30	SEC 25	0.238	19.000	48.710	0.390	143.794	5.854	24.562	72.124
31	SEC 26	0.264	19.000	41.561	0.457	62.877	14.313	4.392	31.934
32	WEC 58	0.020	-	101.010	-	-	-	-	-
33	WEC 5C	0.094	-	50.160	-	-	-	-	-
34	LDW3WB	0.020	-	72.463	-	-	-	-	-
35	LDW4WB	0.104	-	55.853	-	-	-	-	-
36	JP 5	0.032	21.000	372.093	0.056	678.271	4.561	148.695	78.808
37	A62/5	0.632	71.000	128.874	0.550	-709.026	289.982	-2.445	-218.899
38	EC 7	0.328	23.000	62.239	0.369	-1380.688	291.563	-4.735	-964.080

Table 13.
Cobalt.

TABLE 14 NICKEL

REF	SAMPLE	X	CW	CF	CWCF	CO	CI	COCI	PER
1	A62/2	0.475	34.000	33.991	1.000	33.990	34.004	0.999	33.050
2	A62/5	0.746	177.000	144.182	1.227	134.119	189.038	0.709	16.609
3	A76/3	0.475	68.000	51.833	1.311	49.395	79.696	0.619	28.038
4	A76/5	0.509	116.000	66.310	1.749	51.482	132.321	0.389	8.960
5	A76/6	0.237	22.000	17.274	1.273	13.553	26.911	0.503	22.653
6	A78/3	1.763	53.000	102.274	0.518	110.755	14.174	7.813	84.006
7	A78/4	0.237	80.000	116.404	0.687	118.590	70.176	1.689	30.077
8	A78/9	0.576	31.000	37.233	0.832	41.542	27.659	1.501	32.242
9	A78/10	0.949	32.000	69.738	0.458	85.777	14.169	6.053	66.745
10	A78/11	5.294	36.000	420.292	0.085	473.366	-315.107	-1.502	585.528
11	AEC 1	0.271	-	16.591	-	-	-	-	-
12	BEC 4265	0.678	-	150.532	-	-	-	-	-
13	BEC 4270	0.170	-	68.548	-	-	-	-	-
14	EC 7	0.576	58.000	103.634	0.559	108.523	48.333	2.245	30.049
15	EC 11	0.102	71.000	163.987	0.432	284.954	28.321	10.061	66.743
16	EC 15	0.070	14.000	83.532	0.167	121.477	-49.883	-2.435	323.477
17	EC 16	0.271	12.000	30.178	0.397	73.722	-14.819	-4.974	186.087
18	EC DAN 3	0.237	38.000	43.807	0.867	45.129	36.855	1.224	16.424
19	EC DAN 5	0.271	49.000	36.229	1.352	30.844	53.001	0.581	11.368
20	GB45/64/7	0.170	43.000	54.105	0.794	57.257	40.905	1.399	17.057
21	GB45/64/10	0.576	39.000	60.516	0.644	75.566	34.229	2.207	22.359
22	GB47/64/8	0.475	35.000	87.252	0.401	124.109	23.386	5.306	40.885
23	GB47/64/10	0.237	56.000	49.478	1.131	48.191	57.168	0.842	11.204
24	GB48/65/5	0.610	63.000	74.372	0.847	75.064	61.146	1.227	15.870
25	GB48/65/9	0.070	60.000	54.432	1.102	53.770	61.248	0.877	14.966
26	GB48/65/12	0.102	37.000	34.205	1.081	34.054	38.137	0.892	25.642
27	SEC 1	0.305	11.000	22.904	0.480	24.804	8.460	2.932	35.042
28	SEC 9	0.203	24.000	51.575	0.465	95.170	12.037	7.906	57.062
29	SEC 13	0.237	7.000	13.328	0.525	17.761	3.291	5.396	65.033
30	SEC 25	0.305	29.000	62.423	0.464	169.389	14.211	11.919	55.664
31	SEC 26	0.271	49.000	42.663	1.148	36.677	50.316	0.728	7.223
32	WEC 5B	0.070	-	353.535	-	-	-	-	-
33	WEC 5C	0.203	-	108.324	-	-	-	-	-
34	LDW3WB	0.070	-	253.623	-	-	-	-	-
35	LDW4WB	0.070	-	37.593	-	-	-	-	-
36	JP 5	0.070	215.000	813.953	0.264	1336.285	186.956	7.147	15.165
37	A62/5	1.017	177.000	207.381	0.853	-232.482	291.957	-0.796	-28.790
38	EC 7	0.373	58.000	70.778	0.819	-399.103	145.456	-2.743	-110.510

Table 14. Nickel.

TABLE 15 COPPER

REF	SAMPLE	X	CW	CF	CWCF	CO	CI	COCI	PER
1	A62/2	50.000	28.000	3578.074	0.007	4038.464	-1952.668	-2.068	4768.272
2	A62/5	0.433	39.000	83.687	0.466	97.389	22.607	4.307	54.738
3	A76/3	0.211	22.000	23.024	0.955	23.179	21.258	1.090	40.669
4	A76/5	0.544	27.000	70.870	0.380	83.961	12.590	6.668	62.784
5	A76/6	0.622	24.000	45.335	0.529	62.130	1.825	34.029	95.189
6	A78/3	2.689	36.000	155.992	0.230	176.645	-58.547	-3.017	197.254
7	A78/4	6.434	41.000	3160.117	0.012	3347.393	-800.635	-4.180	1656.551
8	A78/9	1.778	40.000	114.932	0.348	166.735	-0.153	-1085.641	100.291
9	A78/10	54.200	40.000	3982.951	0.010	5658.753	-1822.942	-3.104	3522.573
10	A78/11	1.805	21.000	143.299	0.146	160.190	-90.738	-1.765	339.679
11	AEC 1	1.526	-	93.424	-	-	-	-	-
12	BEC 4265	32.451	-	7204.928	-	-	-	-	-
13	BEC 4270	0.166	-	66.935	-	-	-	-	-
14	EC 7	15.440	38.000	2777.978	0.013	3071.534	-542.397	-5.662	1298.127
15	EC 11	4.268	19.000	6861.737	0.002	15763.501	-3121.590	-5.049	13797.209
16	EC 15	0.050	11.000	59.665	0.184	86.223	-33.712	-2.557	292.220
17	EC 16	12.800	10.000	1425.389	0.007	4815.839	-2078.207	-2.317	14587.175
18	EC DAN 3	0.255	27.000	47.134	0.572	51.715	23.033	2.245	26.489
19	EC DAN 5	0.555	35.000	74.197	0.471	90.727	22.717	3.993	46.815
20	GB45/64/7	0.189	25.000	60.152	0.415	70.129	18.369	3.817	35.934
21	GB45/64/10	11.816	28.000	1241.437	0.022	2090.152	-241.016	-8.672	861.441
22	GB47/64/8	0.255	26.000	46.840	0.555	61.541	21.368	2.880	27.291
23	GB47/64/10	0.444	27.000	92.693	0.291	105.656	15.225	6.939	50.950
24	GB48/65/5	8.108	17.000	988.539	0.017	1047.676	-141.382	-7.410	820.885
25	GB48/65/9	0.050	28.000	38.880	0.720	40.173	25.559	1.571	23.960
26	GB48/65/12	0.144	14.000	48.289	0.289	50.137	0.043	1144.840	99.774
27	SEC 1	0.500	13.000	37.548	0.346	41.467	7.762	5.342	49.569
28	SEC 9	1.318	27.000	334.857	0.080	821.573	-106.558	-7.710	437.868
29	SEC 13	0.578	12.000	32.504	0.369	46.871	-0.017	-2658.306	100.109
30	SEC 25	2.523	440.000	516.373	0.852	760.794	406.207	1.872	16.478
31	SEC 26	2.077	17.000	326.983	0.051	619.843	-47.387	-13.080	351.852
32	WEC 5B	0.050	-	252.525	-	-	-	-	-
33	WEC 5C	1.049	-	559.765	-	-	-	-	-
34	LOW3WB	0.050	-	181.159	-	-	-	-	-
35	LOW4WB	0.322	-	172.932	-	-	-	-	-
36	JP 5	0.050	32.000	581.395	0.055	1060.508	6.276	168.958	80.863
37	A62/5	0.211	39.000	43.026	0.906	-15.263	54.233	-0.281	-8.578
38	EC 7	9.429	38.000	1789.184	0.021	*********	12023.611	-5.206	*********

Table 15
Copper

TABLE 16 SILVER

REF	SAMPLE	X	CW	CF	CWCF	CO	CI	COCI	PER
1	A62/2	0.080	-	5.724	-	-	-	-	-
2	A62/5	0.080	-	15.461	-	-	-	-	-
3	A76/3	0.080	-	8.729	-	-	-	-	-
4	A76/5	0.080	-	10.422	-	-	-	-	-
5	A76/6	0.080	-	5.830	-	-	-	-	-
6	A78/3	0.080	-	4.640	-	-	-	-	-
7	A78/4	0.080	-	39.292	-	-	-	-	-
8	A78/9	0.080	-	5.171	-	-	-	-	-
9	A78/10	0.080	-	5.878	-	-	-	-	-
10	A78/11	0.080	-	6.351	-	-	-	-	-
11	AEC 1	0.080	-	4.897	-	-	-	-	-
12	BEC 4265	0.080	-	17.761	-	-	-	-	-
13	BEC 4270	0.080	-	32.258	-	-	-	-	-
14	EC 7	0.080	-	14.393	-	-	-	-	-
15	EC 11	0.080	-	128.617	-	-	-	-	-
16	EC 15	0.080	-	95.465	-	-	-	-	-
17	EC 16	0.080	-	8.908	-	-	-	-	-
18	EC DAN 3	0.080	-	14.787	-	-	-	-	-
19	EC DAN 5	0.080	-	10.695	-	-	-	-	-
20	GB45/64/7	0.080	-	25.461	-	-	-	-	-
21	GB45/64/10	0.080	-	8.405	-	-	-	-	-
22	GB47/64/8	0.080	-	14.695	-	-	-	-	-
23	GB47/64/10	0.080	-	16.701	-	-	-	-	-
24	GB48/65/5	0.080	-	9.753	-	-	-	-	-
25	GB48/65/9	0.080	-	62.208	-	-	-	-	-
26	GB48/65/12	0.080	-	26.827	-	-	-	-	-
27	SEC 1	0.080	-	6.007	-	-	-	-	-
28	SEC 9	0.080	-	20.325	-	-	-	-	-
29	SEC 13	0.080	-	4.498	-	-	-	-	-
30	SEC 25	0.130	-	26.606	-	-	-	-	-
31	SEC 26	0.080	-	12.594	-	-	-	-	-
32	WEC 5B	0.080	-	404.040	-	-	-	-	-
33	WEC 5C	0.080	-	42.689	-	-	-	-	-
34	LDW3WB	0.080	-	289.855	-	-	-	-	-
35	LDW4WB	0.080	-	42.964	-	-	-	-	-
36	JP 5	0.080	-	930.232	-	-	-	-	-
37	A62/5	0.080	-	16.313	-	-	-	-	-
38	EC 7	0.080	-	15.180	-	-	-	-	-

Table 16
Silver.

TABLE 17 GOLD

REF	SAMPLE	X	CW	CF	CWCF	CD	CI	COCI	PER
1	A62/2	0.030	-	2.146	-	-	-	-	-
2	A62/5	0.110	-	21.260	-	-	-	-	-
3	A76/3	0.030	-	3.273	-	-	-	-	-
4	A76/5	0.030	-	3.908	-	-	-	-	-
5	A76/6	0.140	-	10.204	-	-	-	-	-
6	A78/3	0.050	-	2.900	-	-	-	-	-
7	A78/4	0.005	-	2.455	-	-	-	-	-
8	A78/9	0.180	-	11.635	-	-	-	-	-
9	A78/10	0.260	-	19.106	-	-	-	-	-
10	A78/11	0.005	-	0.396	-	-	-	-	-
11	AEC 1	0.450	-	27.549	-	-	-	-	-
12	BEC 4265	0.180	-	39.964	-	-	-	-	-
13	BEC 4270	0.010	-	4.032	-	-	-	-	-
14	EC 7	0.010	-	1.799	-	-	-	-	-
15	EC 11	0.005	-	8.038	-	-	-	-	-
16	EC 15	0.005	-	5.966	-	-	-	-	-
17	EC 16	0.270	-	30.066	-	-	-	-	-
18	EC DAN 3	0.030	-	5.545	-	-	-	-	-
19	EC DAN 5	0.100	-	13.368	-	-	-	-	-
20	GB45/64/7	0.005	-	1.591	-	-	-	-	-
21	GB45/64/10	0.160	-	16.810	-	-	-	-	-
22	GB47/64/8	0.110	-	20.205	-	-	-	-	-
23	GB47/64/10	0.005	-	1.043	-	-	-	-	-
24	GB48/65/5	0.010	-	1.219	-	-	-	-	-
25	GB48/65/9	0.005	-	3.888	-	-	-	-	-
26	GB48/65/12	0.005	-	1.676	-	-	-	-	-
27	SEC 1	0.110	-	8.260	-	-	-	-	-
28	SEC 9	0.010	-	2.540	-	-	-	-	-
29	SEC 13	0.270	-	15.183	-	-	-	-	-
30	SEC 25	0.620	-	126.893	-	-	-	-	-
31	SEC 26	0.180	-	28.337	-	-	-	-	-
32	WEC 5B	0.005	-	25.252	-	-	-	-	-
33	WEC 5C	0.050	-	26.680	-	-	-	-	-
34	LDW3WB	0.010	-	36.231	-	-	-	-	-
35	LDW4WB	0.010	-	5.370	-	-	-	-	-
36	JP 5	0.030	-	348.837	-	-	-	-	-
37	A62/5	0.420	-	85.644	-	-	-	-	-
38	EC 7	0.180	-	34.155	-	-	-	-	-

Table 17

Gold.

TABLE 18 ZINC

REF	SAMPLE	X	CW	CF	CWCF	CO	CI	COCI	PER
1	A62/2	6.397	68.000	457.778	0.148	508.327	-149.466	-3.400	247.136
2	A62/5	2.110	130.000	407.808	0.318	492.990	28.094	17.547	83.125
3	A76/3	0.974	51.000	106.285	0.479	114.623	11.002	10.418	86.754
4	A76/5	2.203	101.000	286.998	0.351	342.503	39.905	8.582	68.466
5	A76/6	1.058	52.000	77.113	0.674	96.883	25.898	3.740	68.508
6	A78/3	2.235	69.000	129.655	0.532	140.095	21.206	6.606	81.620
7	A78/4	1.147	123.000	563.359	0.218	589.799	4.177	141.189	97.292
8	A78/9	2.398	84.000	155.009	0.541	204.101	45.948	4.441	58.460
9	A78/10	9.429	126.000	692.901	0.181	933.841	-141.846	-6.583	184.544
10	A78/11	0.848	26.000	67.322	0.386	73.030	-11.754	-6.212	125.078
11	AEC 1	1.527	-	93.485	-	-	-	-	-
12	BEC 4265	1.961	-	435.390	-	-	-	-	-
13	BEC 4270	0.177	-	71.370	-	-	-	-	-
14	EC 7	3.287	119.000	591.399	0.201	642.011	18.933	33.908	86.644
15	EC 11	0.378	54.000	607.717	0.088	1328.051	-200.137	-6.635	408.990
16	EC 15	0.050	3.000	59.665	0.050	90.589	-49.062	-1.846	1125.728
17	EC 16	5.661	9.000	630.401	0.014	2118.915	-907.788	-2.334	7131.326
18	EC DAN 3	1.791	94.000	331.053	0.283	384.979	47.298	8.139	56.641
19	EC DAN 5	2.680	68.000	358.288	0.189	480.704	-22.962	-20.934	127.669
20	GB45/64/7	1.237	116.000	393.698	0.294	472.511	63.621	7.426	52.179
21	GB45/64/10	5.661	98.000	594.767	0.164	942.222	-12.132	-77.660	110.951
22	GB47/64/8	0.651	110.000	119.581	0.919	126.339	107.870	1.171	13.242
23	GB47/64/10	1.604	89.000	334.864	0.265	383.382	44.934	8.532	56.085
24	GB48/65/5	2.158	121.000	263.106	0.459	271.756	97.833	2.777	29.915
25	GB48/65/9	0.105	117.000	81.648	1.432	77.446	124.929	0.619	11.054
26	GB48/65/12	0.728	73.000	244.131	0.299	253.355	3.348	75.671	96.691
27	SEC 1	1.284	41.000	96.425	0.425	105.271	29.174	3.608	39.900
28	SEC 9	1.102	65.000	279.979	0.232	619.857	-28.264	-21.930	137.226
29	SEC 13	1.169	43.000	65.740	0.654	81.673	29.671	2.752	48.681
30	SEC 25	0.767	138.000	156.979	0.879	217.719	129.602	1.679	15.035
31	SEC 26	1.378	104.000	216.939	0.479	323.640	80.540	4.018	30.030
32	WEC 5B	0.050	-	252.525	-	-	-	-	-
33	WEC 5C	1.058	-	564.567	-	-	-	-	-
34	LDW3WB	0.395	-	1431.159	-	-	-	-	-
35	LDW4WB	0.395	-	212.137	-	-	-	-	-
36	JP 9	0.050	63.000	581.395	0.108	1033.474	38.728	26.685	40.026
37	A62/5	1.214	130.000	247.553	0.525	-1454.369	574.792	-2.530	-245.229
38	EC 7	5.486	119.000	1040.986	0.114	*********	6429.343	-5.111	-4435.118

Table 18.
Zinc.

TABLE 19 ALUMINIUM

REF	SAMPLE	X	CW	CF	CWCF	CO	CI	COCI	PER
1	A62/2	108.750	9.300	0.778	11.950	-0.326	14.054	-0.023	-1.162
2	A62/5	153.750	13.750	2.971	4.627	-0.333	17.703	-0.018	-0.531
3	A76/3	98.250	8.890	1.072	8.291	-0.106	14.546	-0.007	-0.464
4	A76/5	192.750	11.810	2.511	4.703	-0.263	14.864	-0.017	-0.451
5	A76/6	330.750	8.850	2.410	3.671	-2.658	15.542	-0.171	-11.045
6	A78/3	222.750	8.910	1.292	6.895	-0.018	14.912	-0.001	-0.085
7	A78/4	1.350	11.820	0.066	178.263	-0.639	14.991	-0.042	-1.097
8	A78/9	668.250	11.210	4.319	2.595	-0.443	14.902	-0.029	-0.952
9	A78/10	474.750	12.800	3.488	3.668	-0.468	17.199	-0.027	-0.911
10	A78/11	19.650	6.450	0.156	41.345	-0.713	12.200	-0.058	-4.924
11	AEC 1	*******	9.020	6.212	1.451	1.651	11.242	0.146	4.241
12	BEC 4265	192.750	8.890	4.279	2.077	-7.713	15.194	-0.507	-23.878
13	BEC 4270	149.250	10.190	6.018	1.693	-1.689	12.650	-0.133	-2.844
14	EC 7	51.449	9.980	0.925	10.781	-0.044	11.897	-0.003	-0.071
15	EC 11	4.350	10.390	0.699	14.856	-11.907	14.837	-0.802	-19.058
16	EC 15	36.599	10.290	4.367	2.356	1.135	15.731	0.072	4.113
17	EC 16	729.750	13.880	8.126	1.708	-5.655	22.368	-0.252	-12.342
18	EC DAN 3	101.250	9.950	1.871	5.316	0.033	11.541	0.002	0.047
19	EC DAN 5	234.750	10.760	3.138	3.428	-0.075	13.148	-0.005	-0.127
20	GB45/64/7	44.250	9.670	1.408	6.866	-0.936	11.228	-0.083	-1.240
21	GB45/64/10	428.250	9.870	4.499	2.193	0.742	11.060	0.067	0.868
22	GB47/64/8	255.750	9.720	4.697	2.069	1.155	10.836	0.106	1.370
23	GB47/64/10	68.250	11.560	1.424	8.113	-0.575	13.376	-0.043	-0.647
24	GB48/65/5	46.950	8.880	0.572	15.513	0.066	10.234	0.006	0.100
25	GB48/65/9	11.700	9.520	0.909	10.463	-0.113	11.451	-0.009	-0.199
26	GB48/65/12	9.750	9.860	0.326	30.156	-0.186	13.740	-0.013	-0.527
27	SEC 1	234.899	7.750	1.764	4.393	0.808	9.027	0.089	1.621
28	SEC 9	210.750	8.110	5.354	1.514	0.997	9.305	0.107	1.770
29	SEC 13	567.750	7.250	3.192	2.270	0.350	9.627	0.036	1.238
30	SEC 25	303.750	7.840	6.216	1.261	1.021	8.558	0.119	1.242
31	SEC 26	365.250	10.270	5.750	1.786	1.479	11.208	0.132	1.390
32	WEC 5B	5.100	8.730	2.575	3.389	-1.485	9.096	-0.163	-0.588
33	WEC 5C	51.449	7.000	2.745	2.549	-1.479	7.486	-0.197	-1.147
34	LDW3WB	12.299	8.140	4.456	1.826	4.096	8.598	0.476	5.128
35	LDW4WB	135.750	8.720	7.290	1.196	0.062	9.563	0.006	0.063
36	JP 5	1.350	5.180	1.569	3.299	-1.578	5.349	-0.295	-0.743
37	A62/5	747.750	13.750	15.247	0.901	-6.436	19.417	-0.331	-10.261
38	EC 7	557.250	9.980	10.574	0.943	-11.269	14.045	-0.802	-18.134

Table 19.
Aluminium.

TABLE 20 LEAD

REF	SAMPLE	X	CW	CF	CWCF	CO	CI	COCI	PER
1	A62/2	0.817	35.000	58.465	0.598	61.508	21.907	2.807	58.099
2	A62/5	0.303	31.000	58.562	0.529	67.013	20.889	3.207	47.384
3	A76/3	0.714	38.000	77.913	0.487	83.933	9.123	9.199	85.258
4	A76/5	0.714	26.000	93.017	0.279	113.016	3.986	28.346	87.761
5	A76/6	0.611	34.000	44.533	0.763	52.825	23.052	2.291	57.129
6	A78/3	0.817	27.000	47.395	0.569	50.905	10.929	4.657	75.792
7	A78/4	0.050	39.000	24.557	1.588	23.690	42.896	0.552	12.325
8	A78/9	1.846	34.000	119.327	0.284	178.318	-11.724	-15.209	126.186
9	A78/10	1.537	40.000	112.948	0.354	143.952	5.533	26.013	89.610
10	A78/11	0.303	31.000	24.055	1.288	23.096	37.345	0.618	33.176
11	AEC 1	0.611	-	37.406	-	-	-	-	-
12	BEC 4265	0.303	-	67.273	-	-	-	-	-
13	BEC 4270	0.200	-	80.645	-	-	-	-	-
14	EC 7	0.508	34.000	91.399	0.371	97.549	21.841	4.466	46.077
15	EC 11	0.200	26.000	321.543	0.080	706.018	-109.644	-6.439	451.579
16	EC 15	0.200	50.000	238.663	0.209	341.621	-123.336	-2.769	254.712
17	EC 16	0.920	50.000	102.449	0.488	228.089	-27.382	-8.329	138.176
18	EC DAN 3	0.303	26.000	56.007	0.464	62.833	20.088	3.127	33.422
19	EC DAN 5	0.611	30.000	81.684	0.367	103.480	13.804	7.496	62.294
20	GB45/64/7	0.508	34.000	161.680	0.210	197.917	9.917	19.956	74.568
21	GB45/64/10	0.611	31.000	64.194	0.482	87.411	23.640	3.697	32.539
22	GB47/64/8	0.508	30.000	93.313	0.321	137.974	15.928	8.662	53.028
23	GB47/64/10	0.611	25.000	127.557	0.195	147.795	6.618	22.329	76.972
24	GB48/65/5	0.303	29.000	36.942	0.785	37.425	27.705	1.350	17.189
25	GB48/65/9	0.097	40.000	75.427	0.530	79.638	32.053	2.484	33.249
26	GB48/65/12	0.303	29.000	101.609	0.285	105.523	-0.552	-190.911	101.374
27	SEC 1	0.817	24.000	61.354	0.391	67.316	16.030	4.199	43.587
28	SEC 9	0.303	34.000	76.981	0.441	144.934	15.353	9.440	61.341
29	SEC 13	0.714	25.000	40.152	0.622	50.769	16.119	3.149	52.049
30	SEC 25	0.508	233.000	103.970	2.241	-308.968	290.090	-1.065	-12.637
31	SEC 26	0.405	36.000	63.759	0.564	89.985	30.233	2.976	24.121
32	WEC 5B	0.097	-	489.898	-	-	-	-	-
33	WEC 5C	0.303	-	161.686	-	-	-	-	-
34	LDW3W8	0.097	-	351.449	-	-	-	-	-
35	LDW4W8	0.200	-	107.411	-	-	-	-	-
36	JP 5	0.200	-	2325.582	-	-	-	-	-
37	A62/5	0.508	31.000	103.588	0.299	-947.346	305.658	-3.099	-669.865
38	EC 7	0.405	34.000	76.850	0.442	-1498.863	327.278	-4.579	-707.992

Table 20
Lead

TABLE D EXTREME VALUES.

SAMPLE	Pb	Al	Au	Ag	Cu	Ni	Co	Fe	Mn	Cr	Sr	Ca	Mg	Cs	Rb	K	Na	Li
A78/9	X				X				X				X					
SEC25	X		X					X			X	X	X		X		X	X
EC.16		X				X			X		X	X	X		X	X		
BEC4265		X						X	X		X		X		X	X	X	X
A76/6		X			X		X			X			X	X		X	X	X
JP.5			X	X											X			
A62/5			X											X				
SEC.13					X		X				X	X	X				X	
EC.7					X													
A78/11						X												
SEC26									X							X		
SEC.9									X		X	X	X				X	
AEC1									X			X	X				X	X
BEC4270											X		X					
A78/3											X							

NOTES ON THE FREQUENCY DISTRIBUTION DIAGRAMS.

1) Tables 21-37 are frequency distribution diagrams for the values Co and Ci from Tables 1-20. The organic values Co are shaded "black" and the inorganic values Ci are left "white". When I refer to "black" and "white", in the discussion of the results (Section 3.6 following) I will use this convention. Overlap is shaded grey. Doubtful values are indicated by triangles.

2) When "black" lies to the left of "white", the element has a tendency to concentrate in the inorganic rather than the organic fraction, and vice versa.

3) Any sample lying far off the scale, is indicated with an arrow, and its concentration is given.

4) The corresponding Tables 21A - 37A are Cw and Cf plots from Tables 1-20 in the same manner. Cf is "black" like Co, and Cw "white" like Ci.

5) Because so few Caesium values are available, three graphs are plotted:

Table 25A - the few determined Cs values for Co and Ci.

Table 25B - the maximum Co and minimum Ci values for all samples calculated from the detection limits as in Table 5. These values are relative. The big arrows indicate the direction in which the real values lie.

Table 25C - This plots Cw and Cf in a similar manner to 25B, except that Cw is fixed.

Table 21 Lithium 30 samples

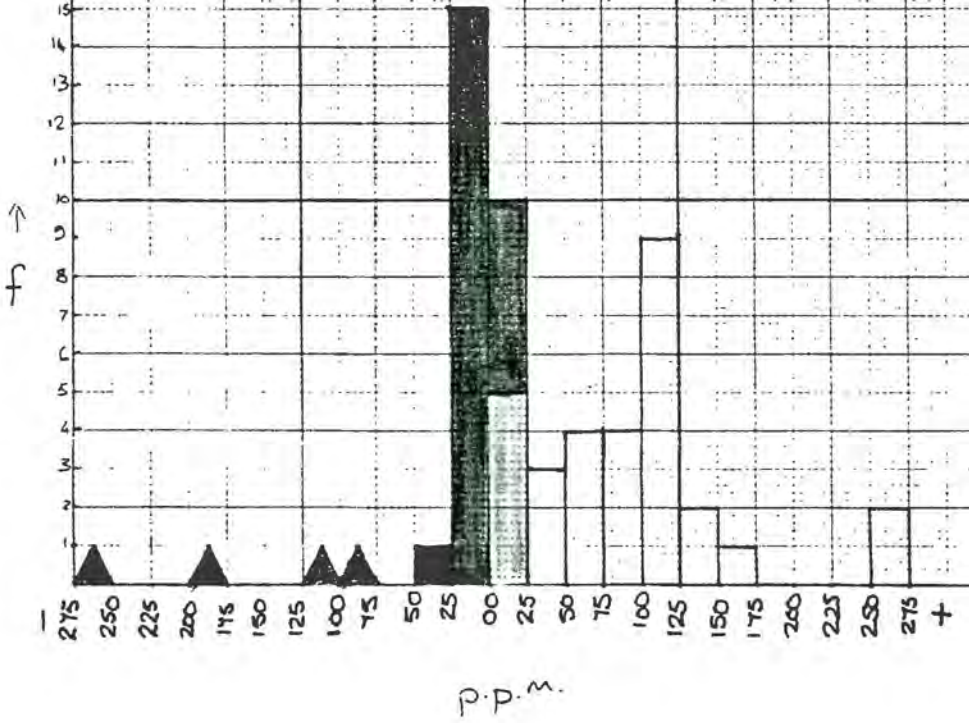


Table 21A Lithium.

Samples: CW 36
CF 33

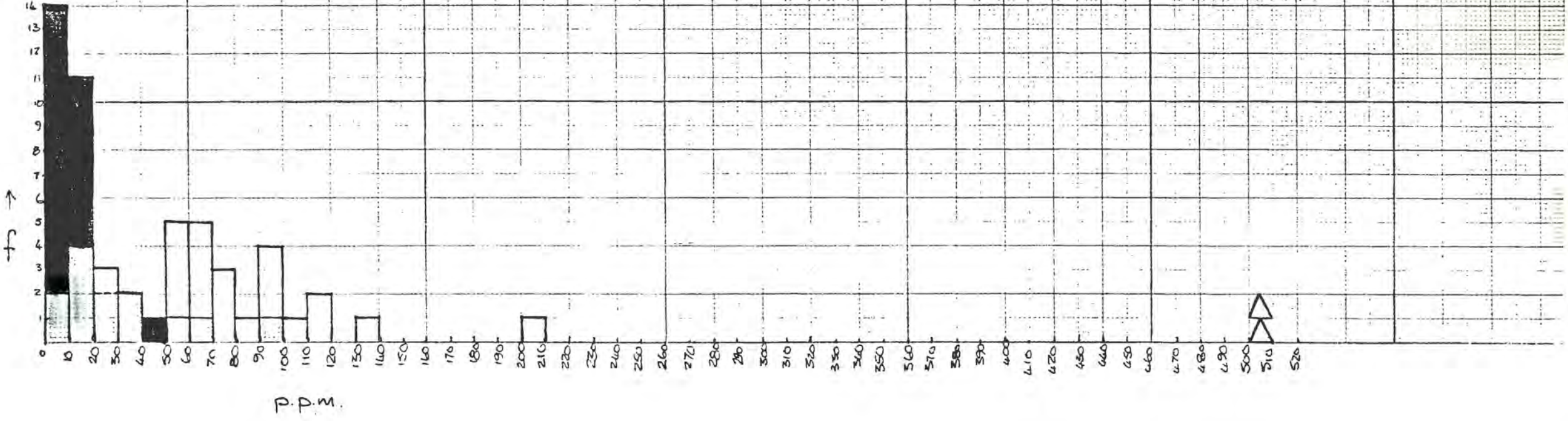


Table 22 Sodium. 36 samples.

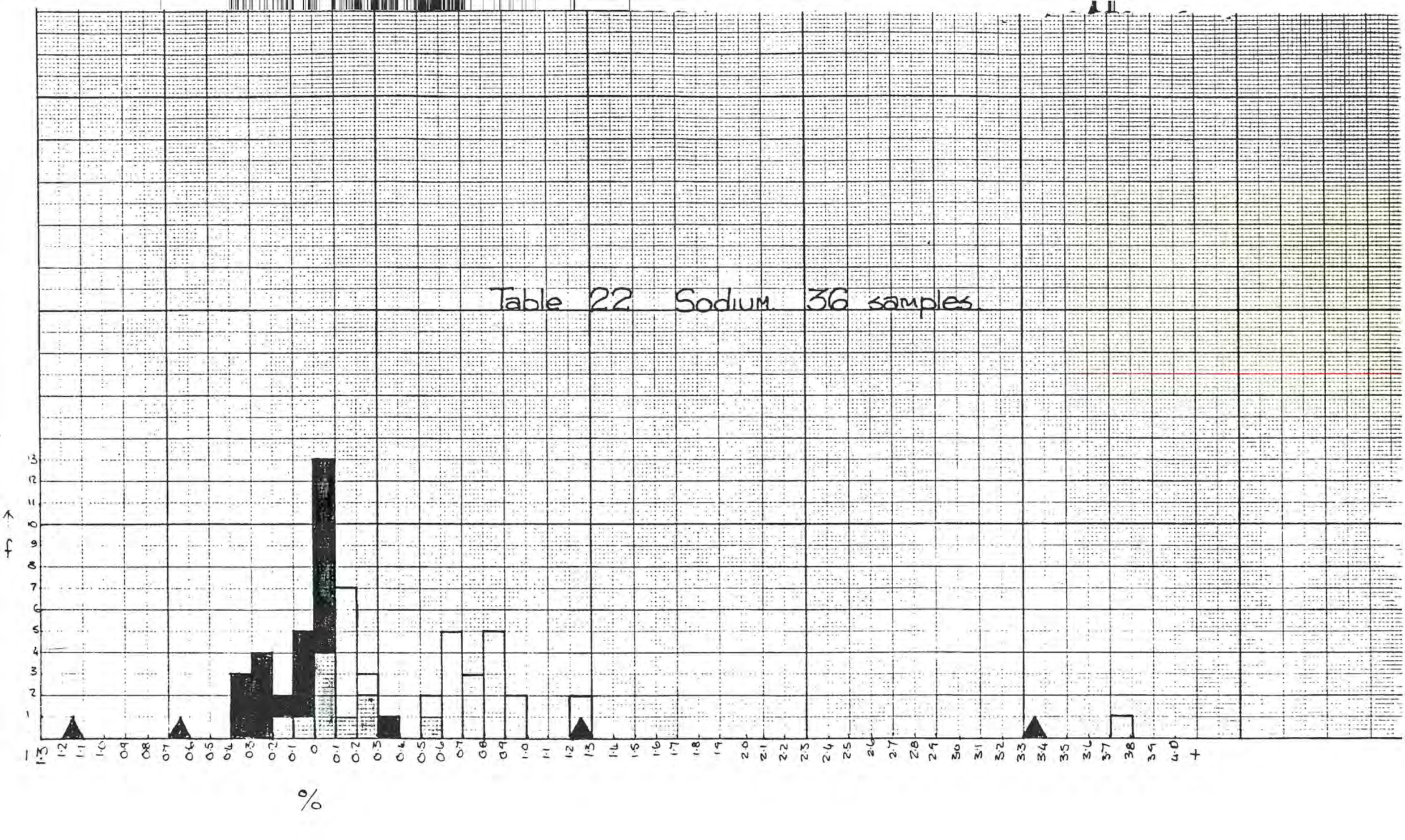


Table 22A Sodium.

CW/CF 36 samples.

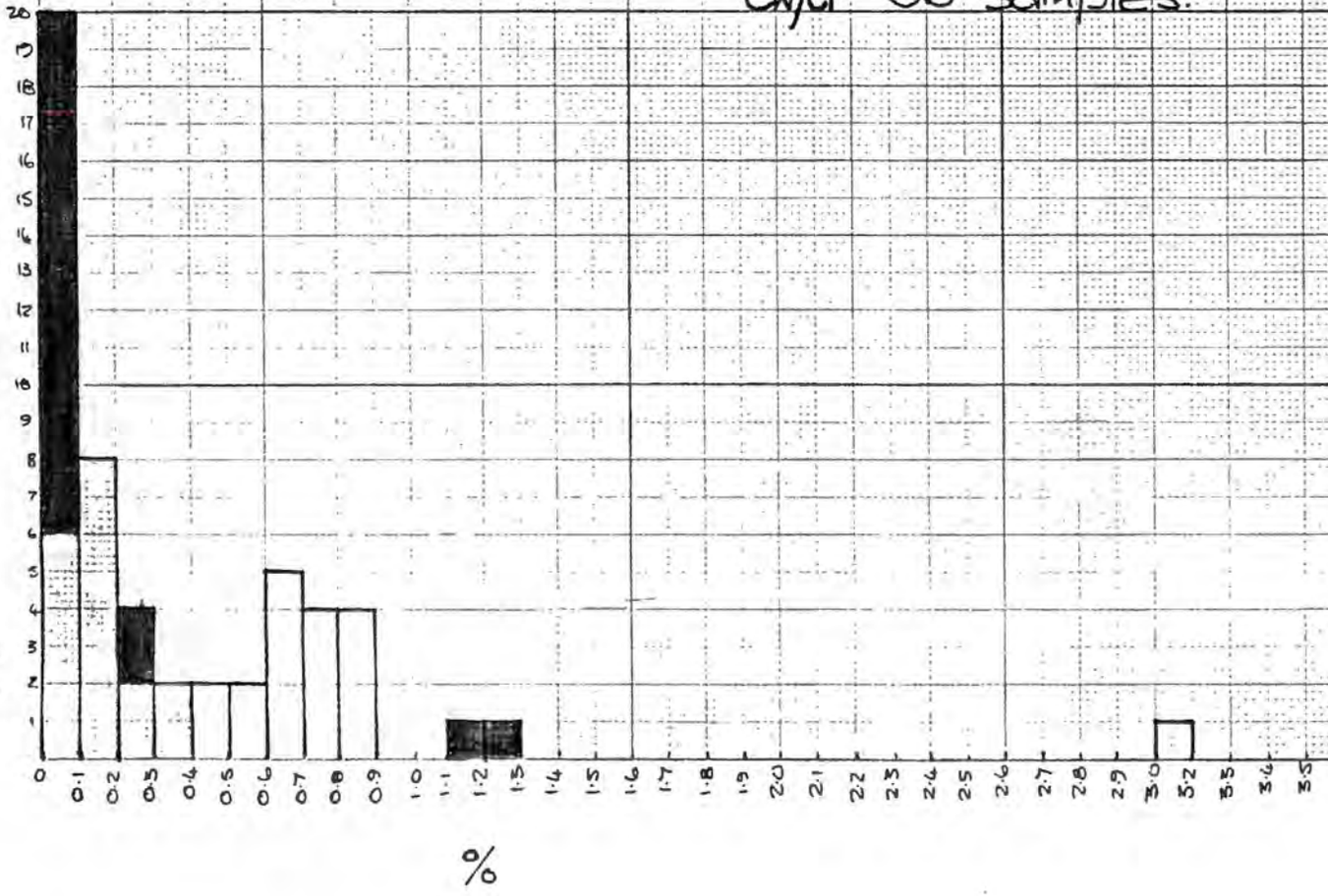


Table 23 Potassium 36 samples

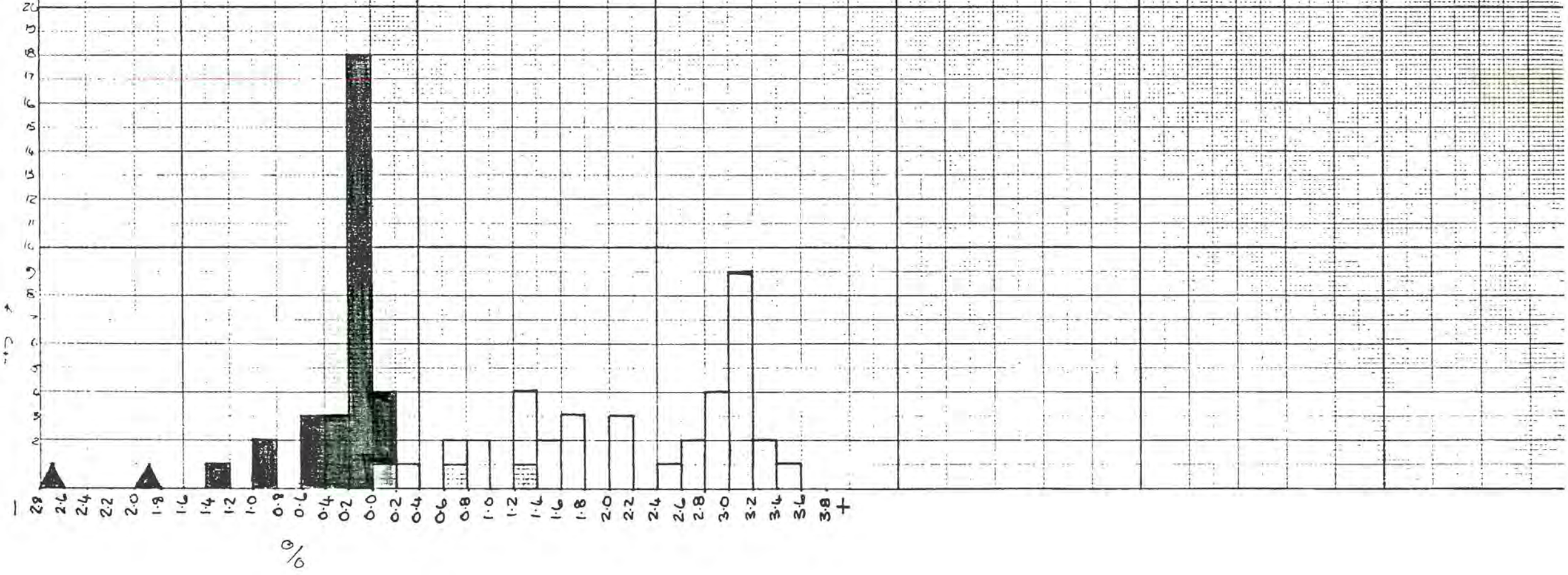


Table 23A Potassium

CW/CF 36 samples.

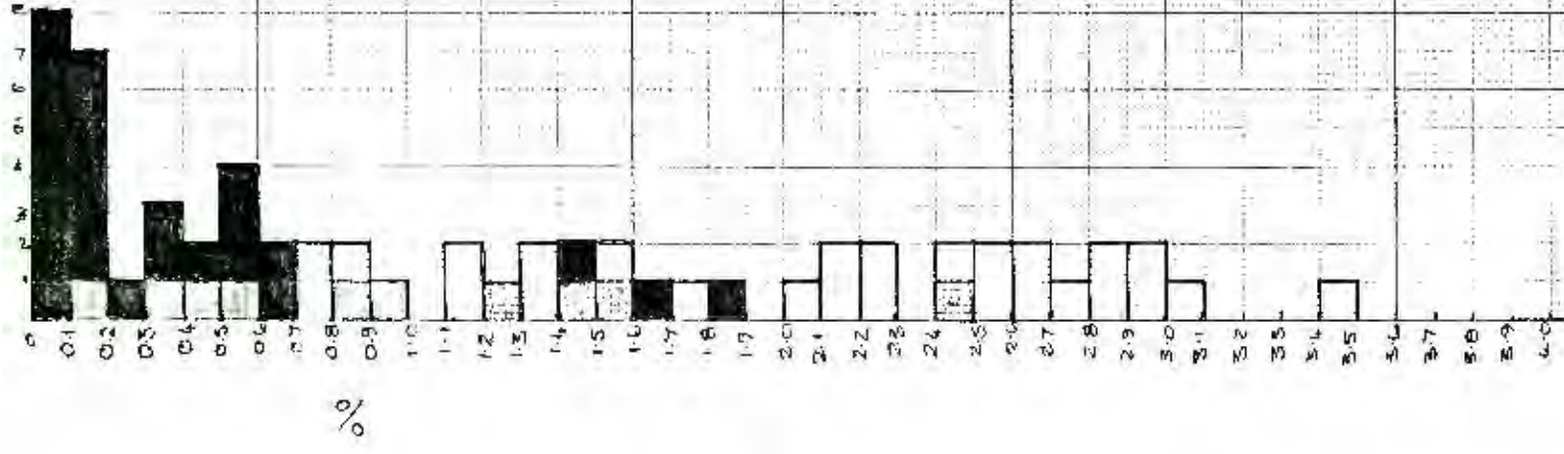


Table 24 Rubidium 18 samples

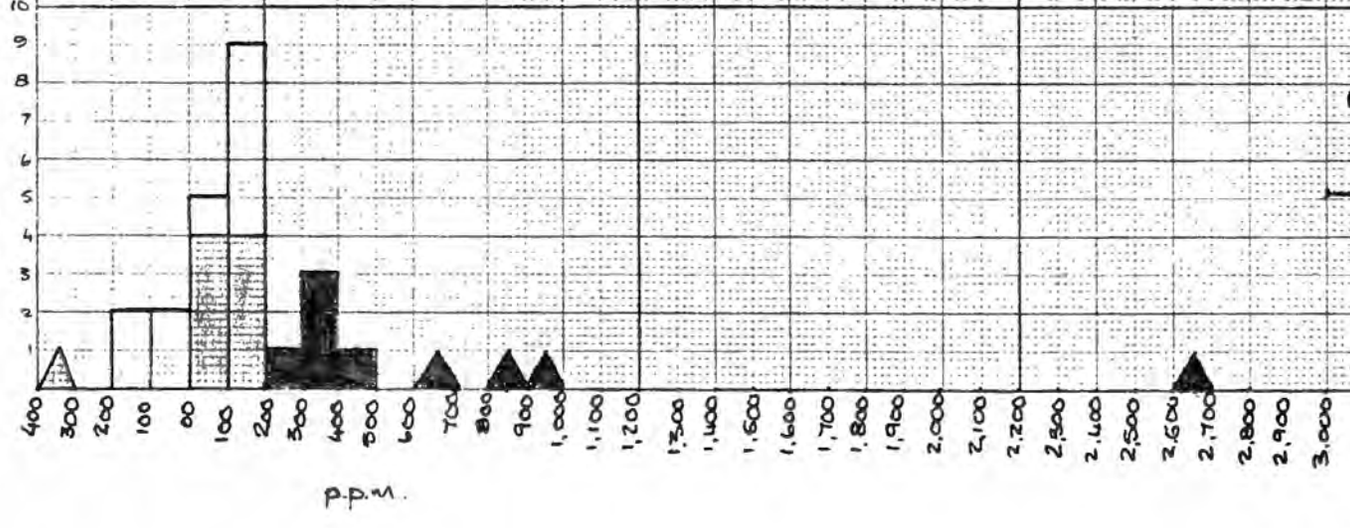


Table 24A Rubidium

samples: CW 29
CF 24

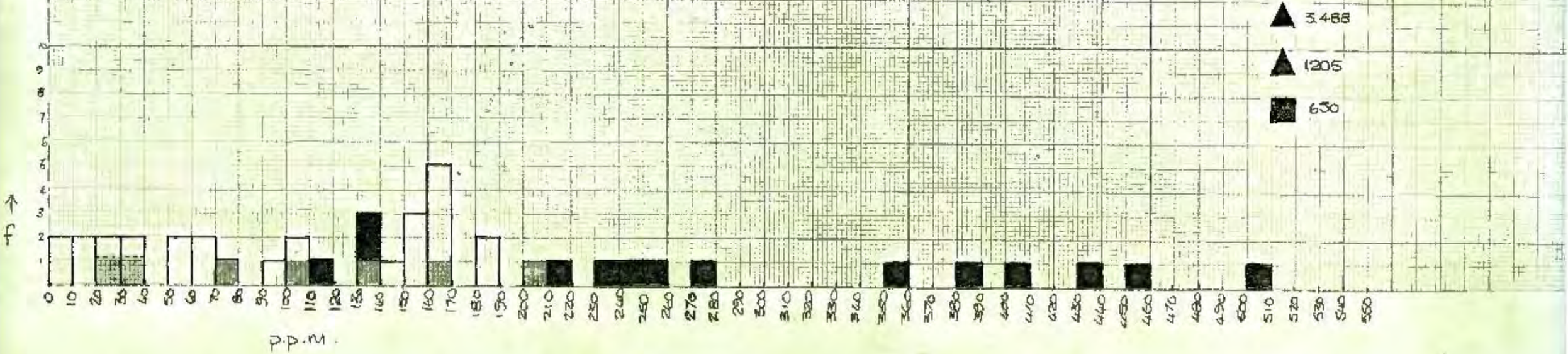


Table 25A Caesium 6 samples.

Absolute Values.

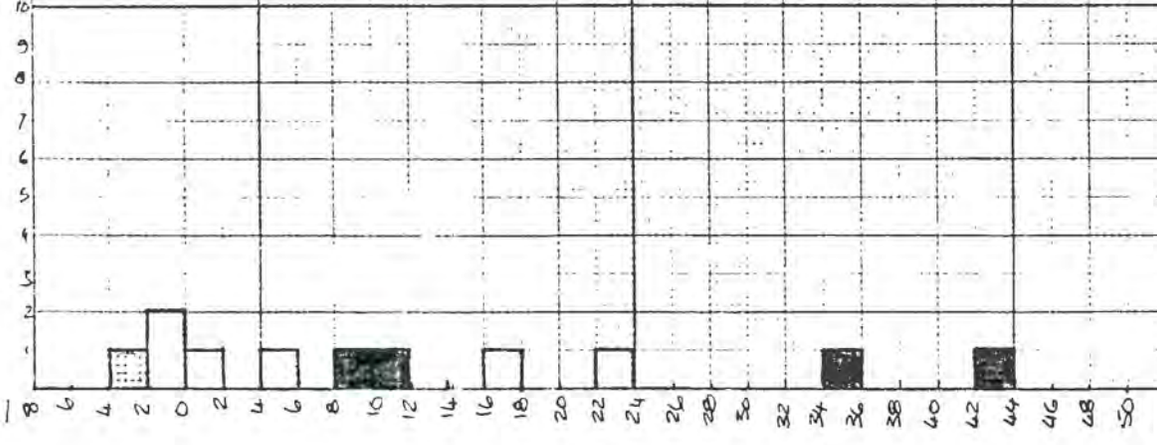


Table 25B. Caesium. 34 Samples.

Relative Values.

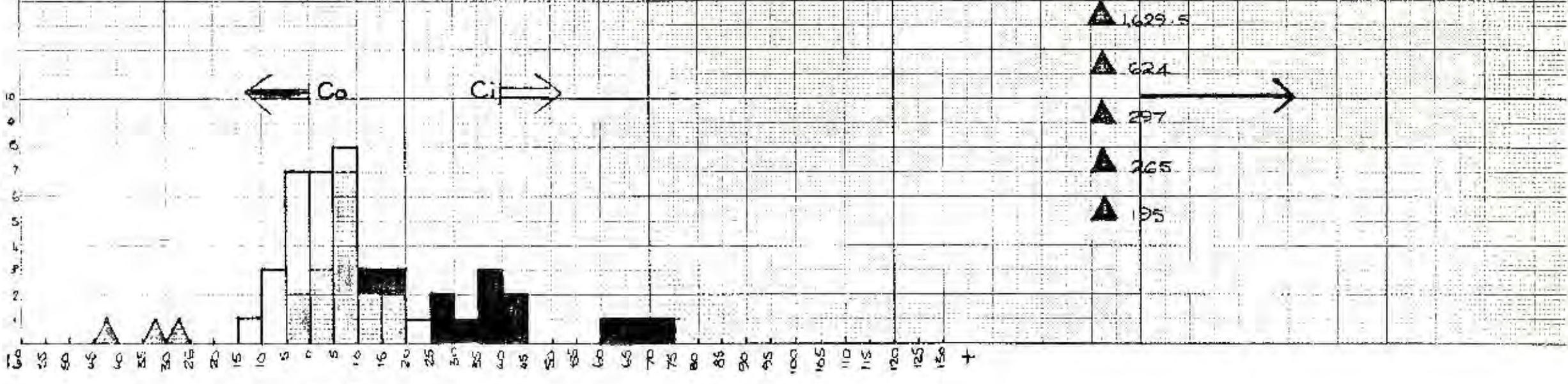


Table 25C Caesium

samples: CW 29
CF 24

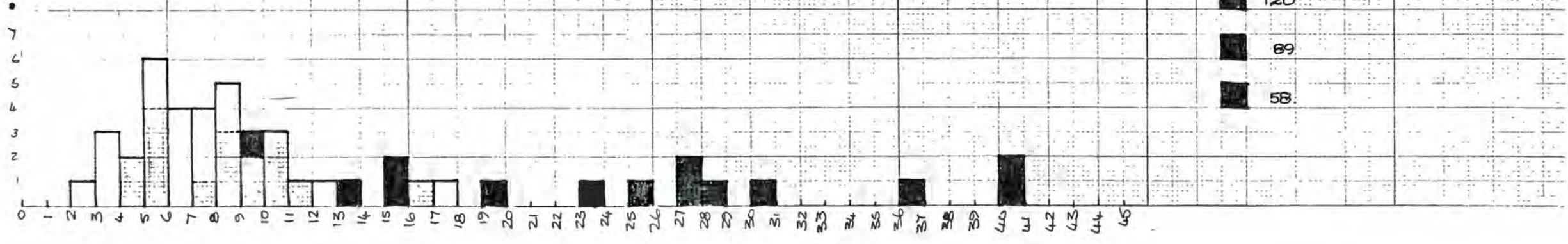


Table 26 Magnesium 36 samples.

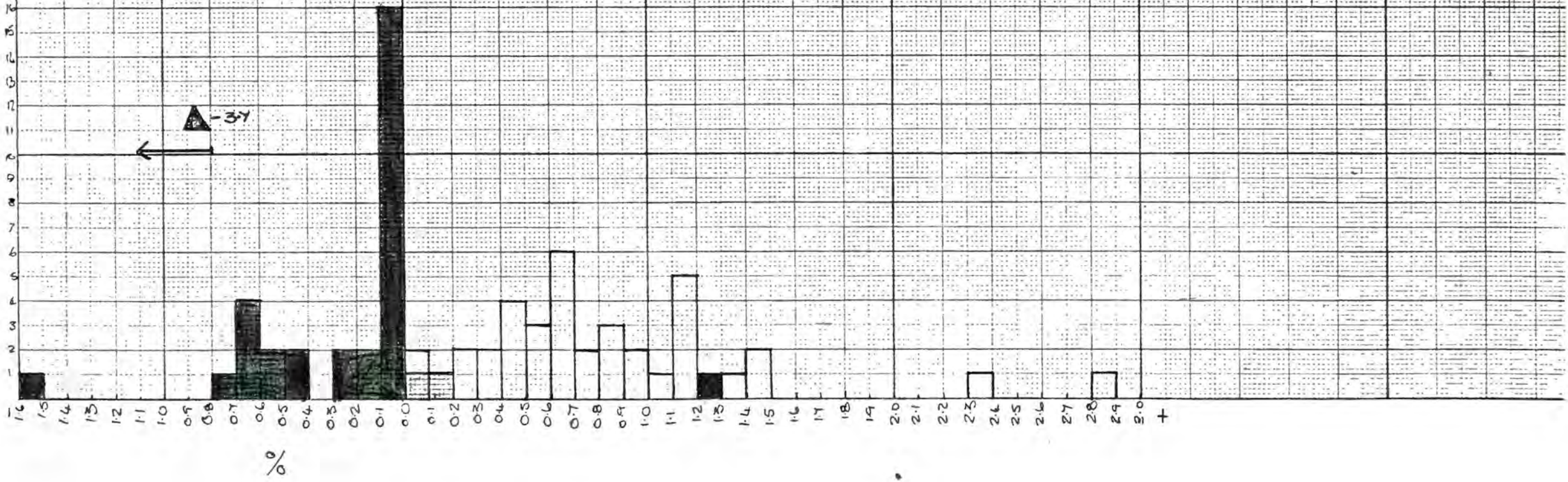


Table 26A Magnesium

samples: CW/CF 36

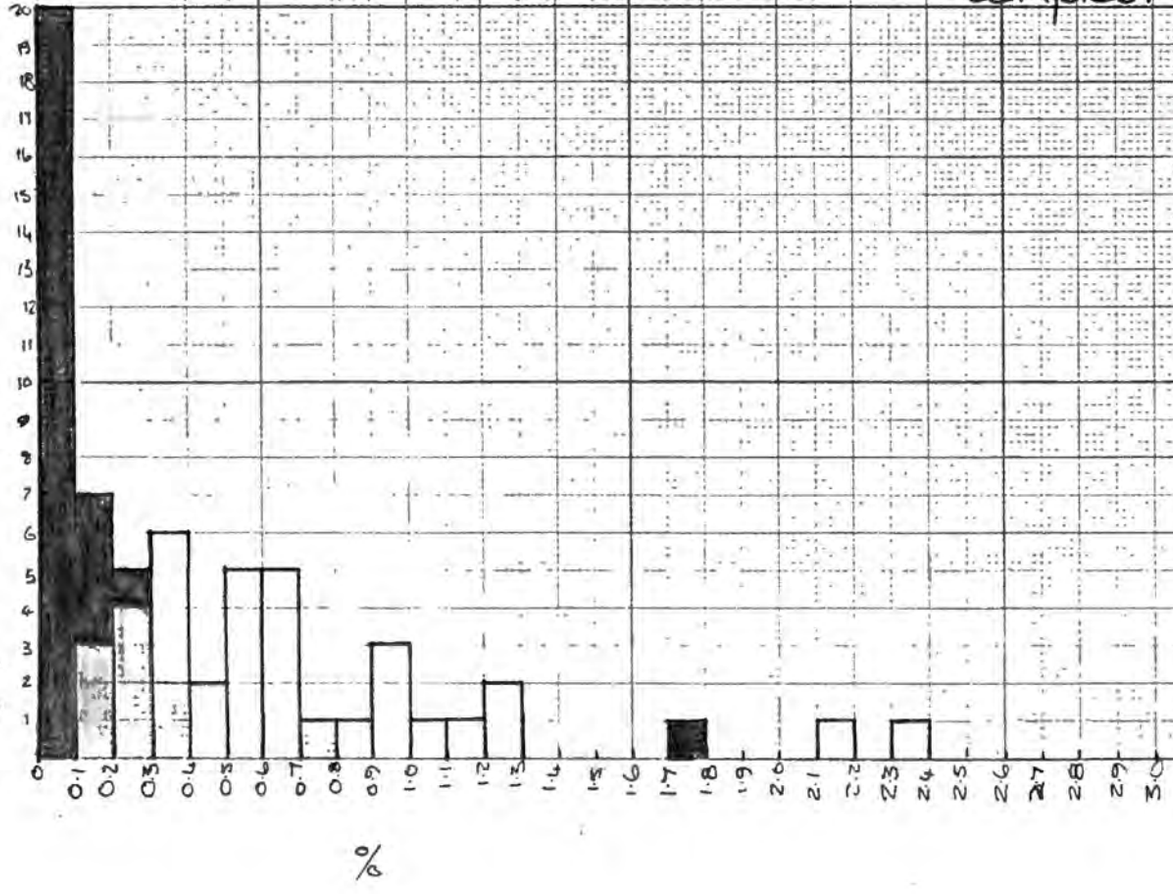
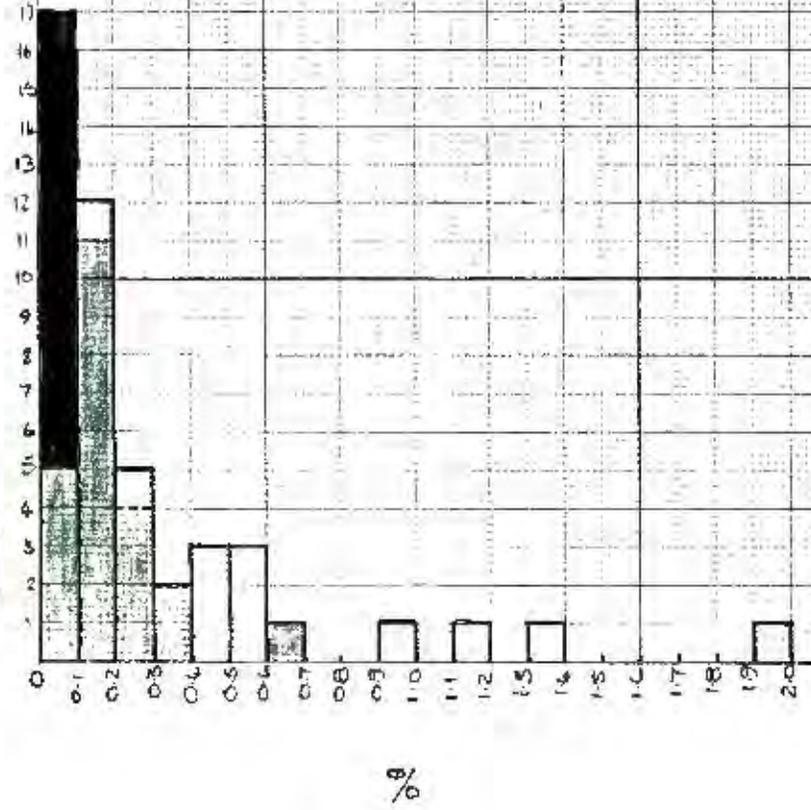


Table 27A Calcium

samples: CW/CF 36



9-2

7-1

Table 28 Strontium 32 Samples.

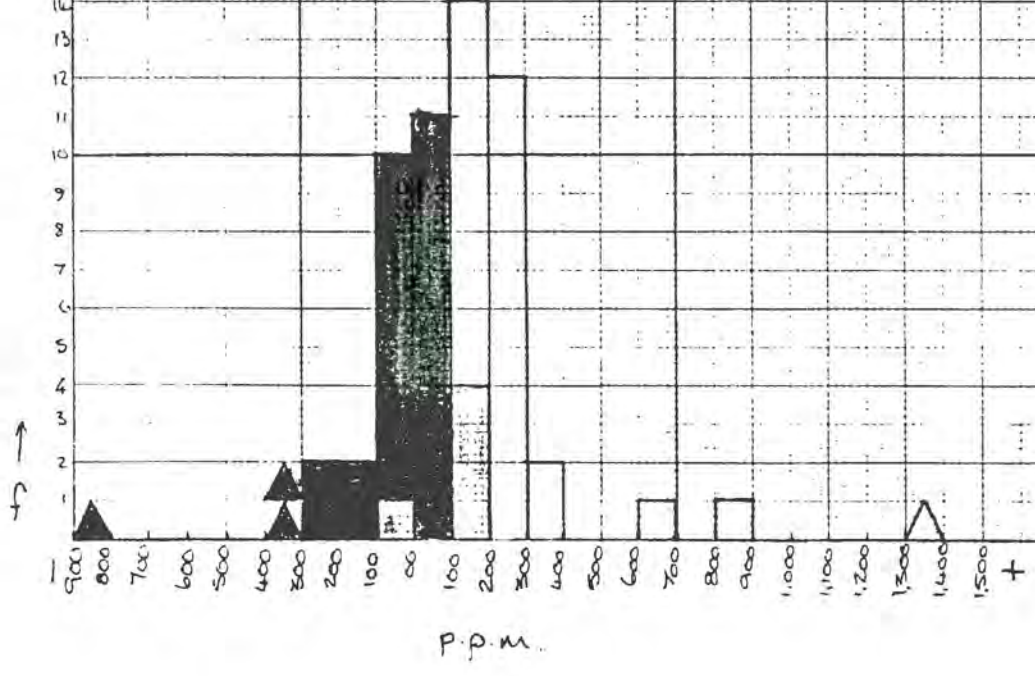


Table 28A Strontium

samples: CF 31
CW 36.

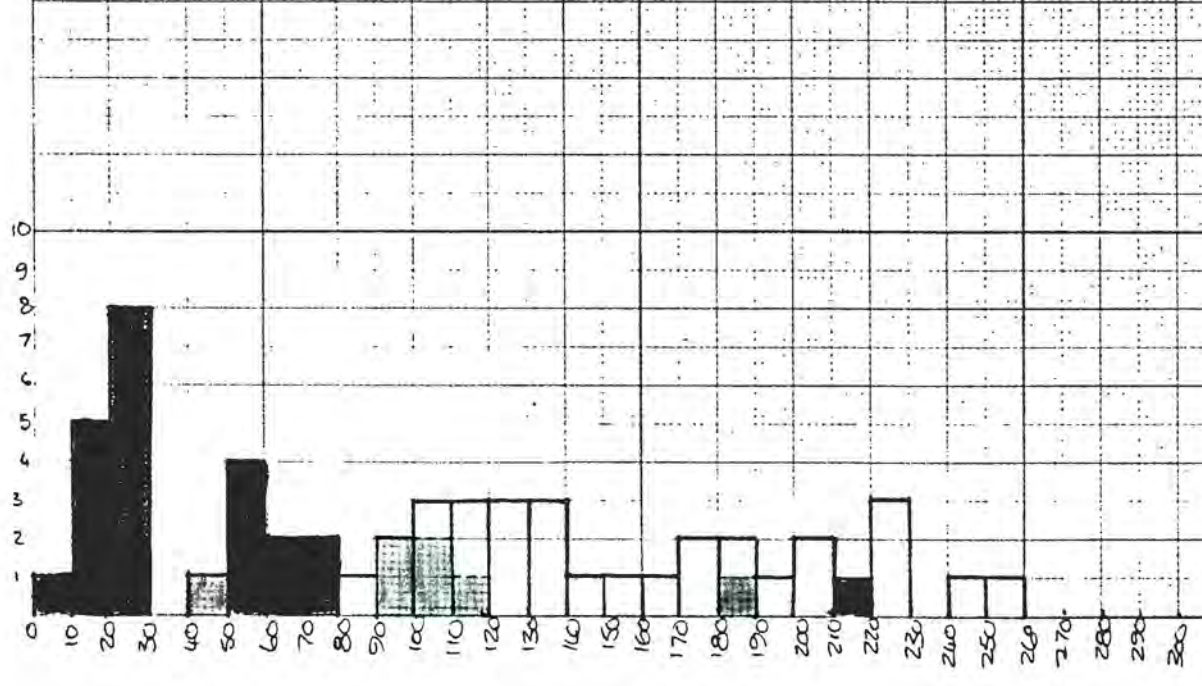


Table 29 Chromium 28 samples.

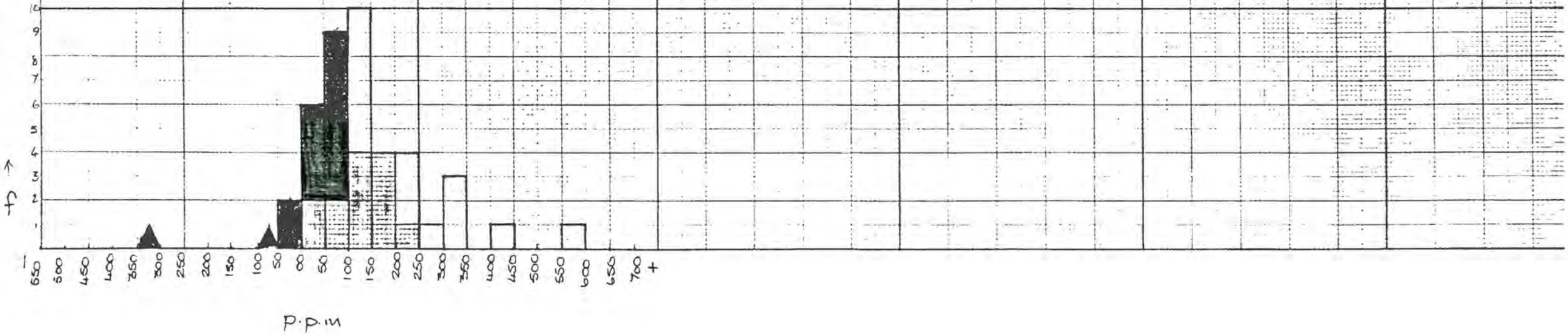


Table 29A Chromium.

samples: CW 29
CF 33

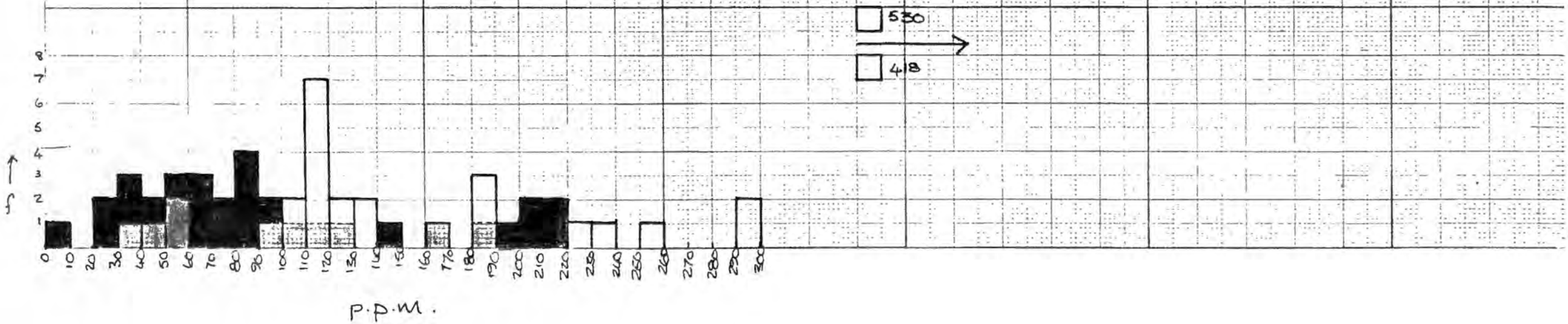


Table 30 Manganese 27 samples.

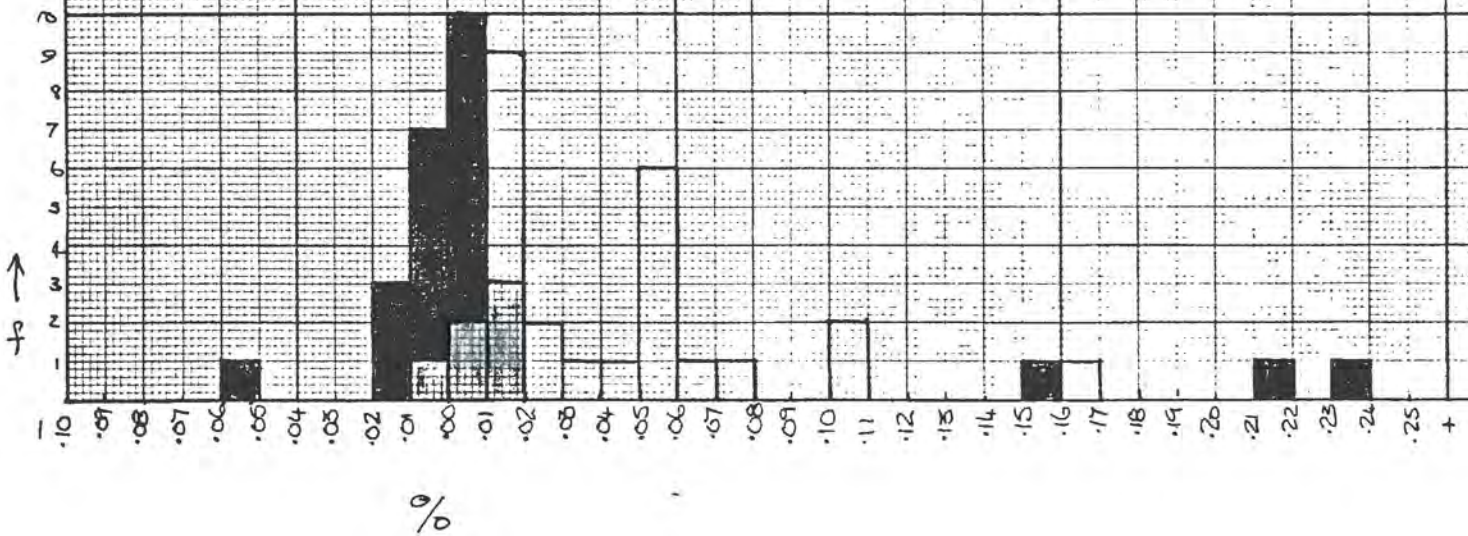


Table 30A Manganese

samples: CW 36
CF 33

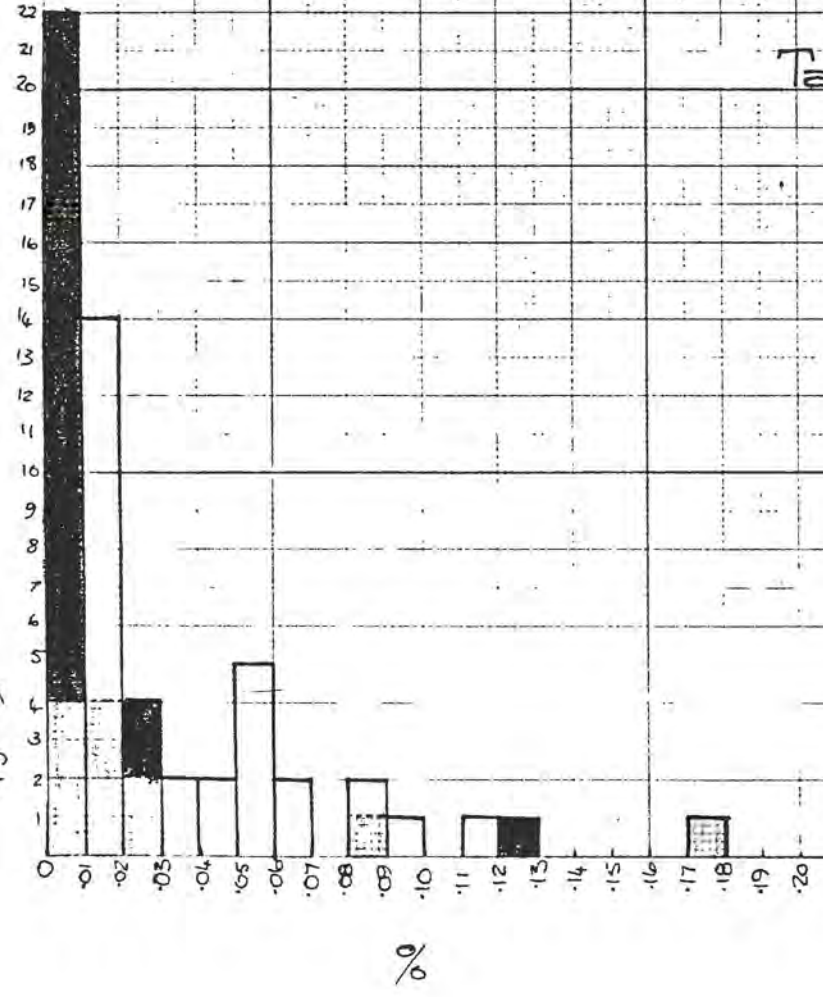


Table 31 Iron 36 samples.

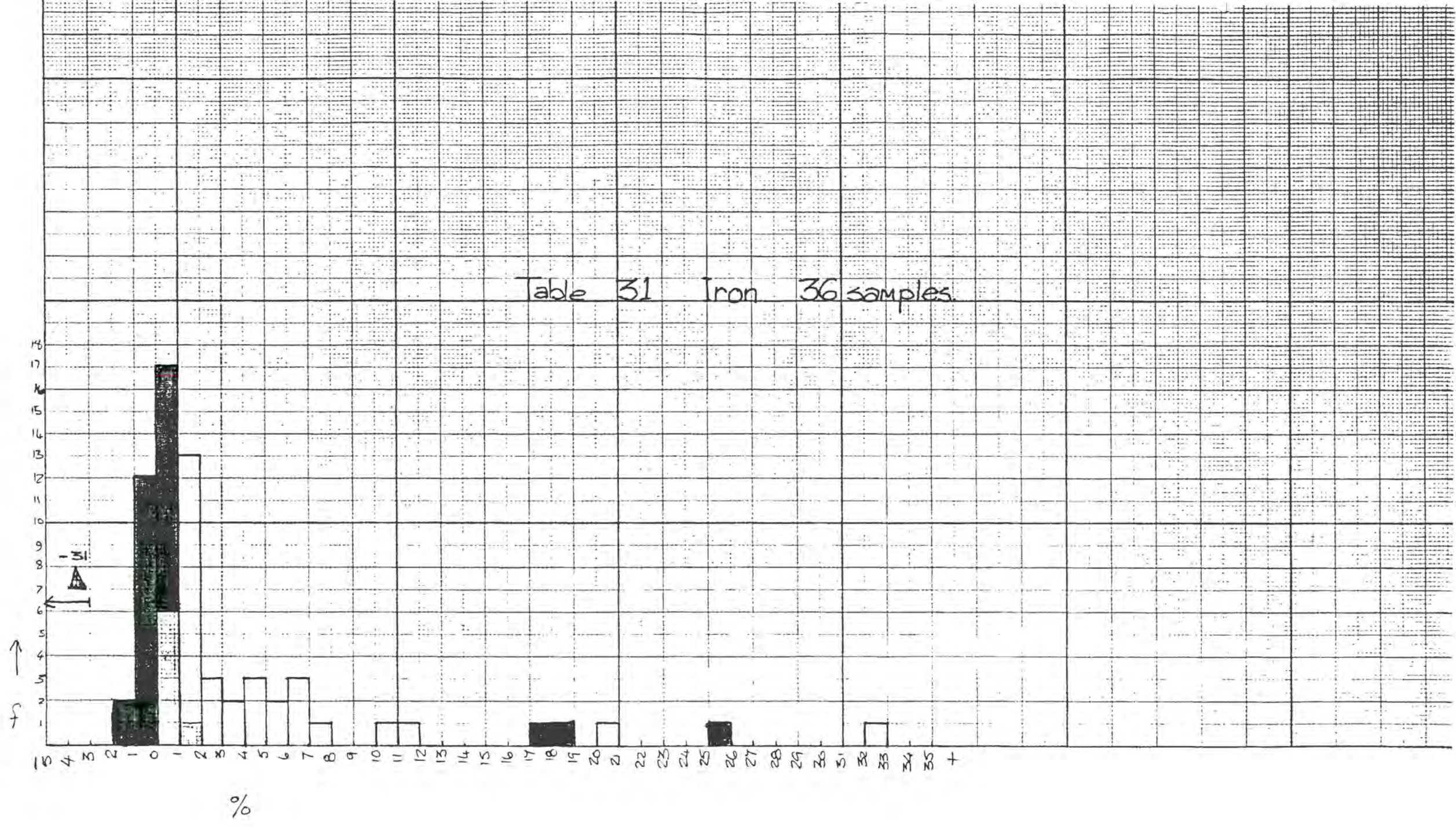


Table 31A Iron

samples: CW/CF 36

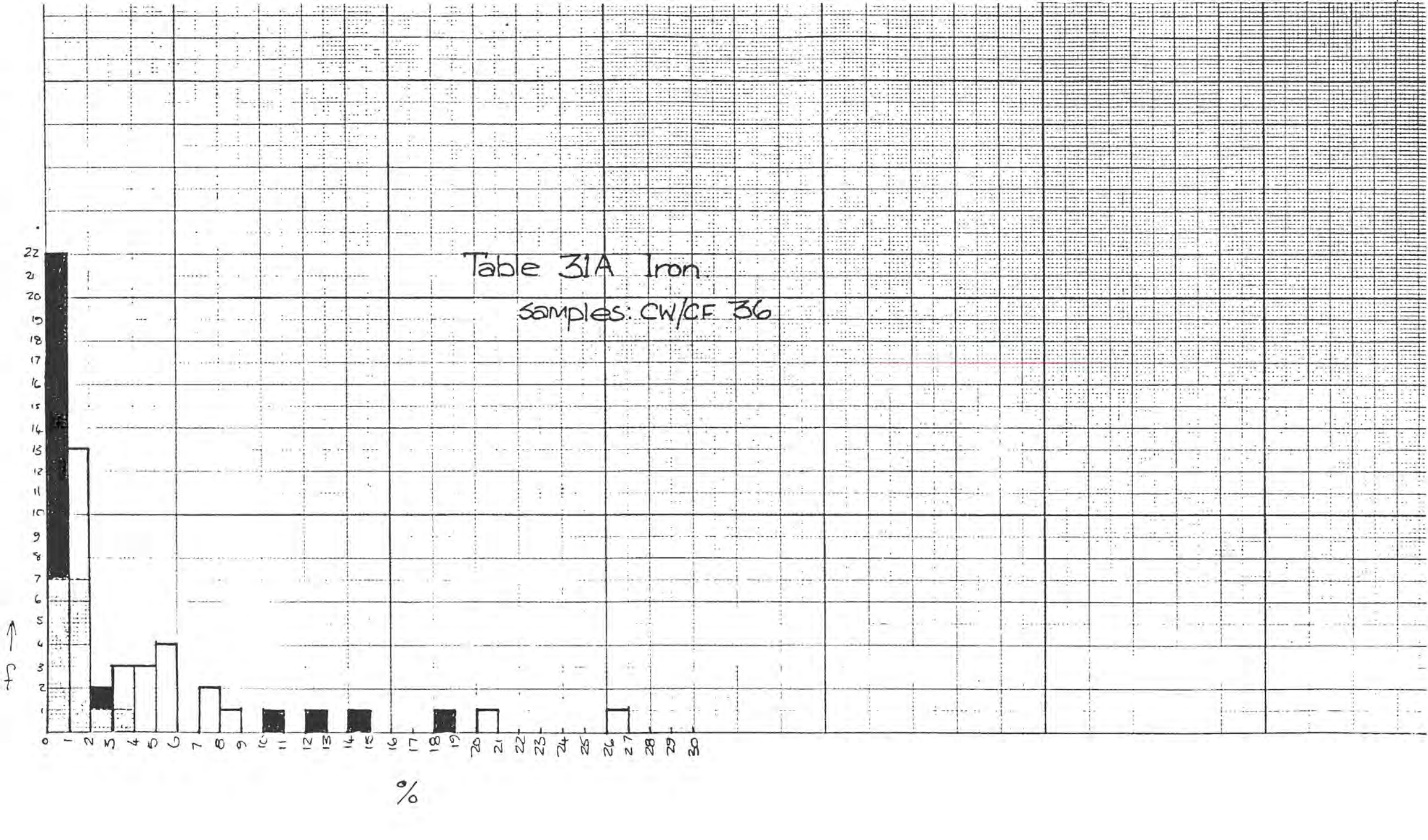


Table 32 Cobalt 27 samples.

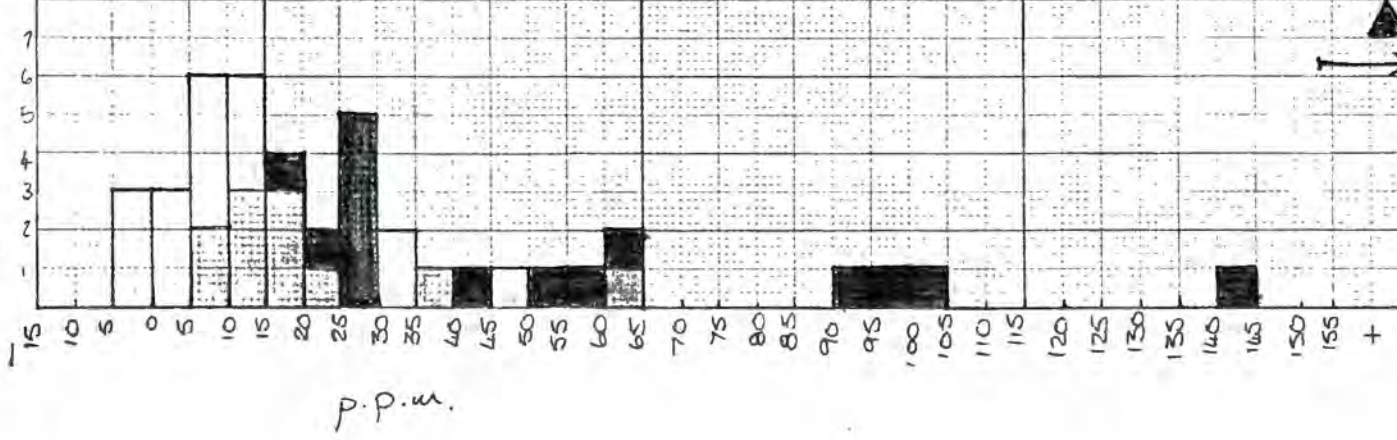


Table 32A Cobalt

samples: CW29
CF36

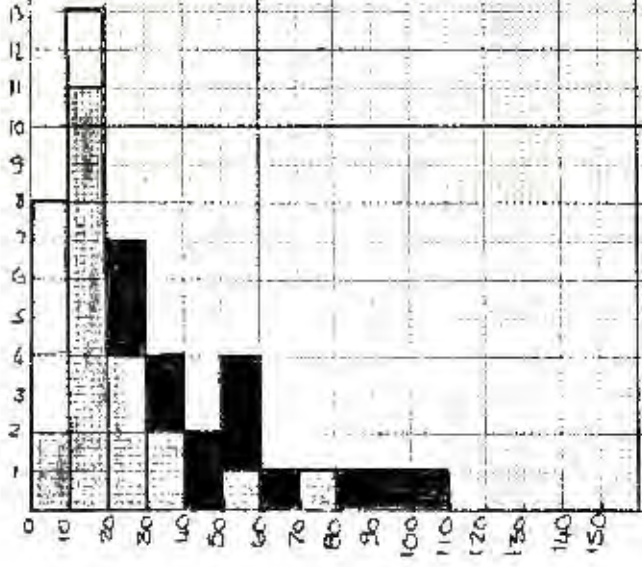


Table 33 Nickel 26 samples

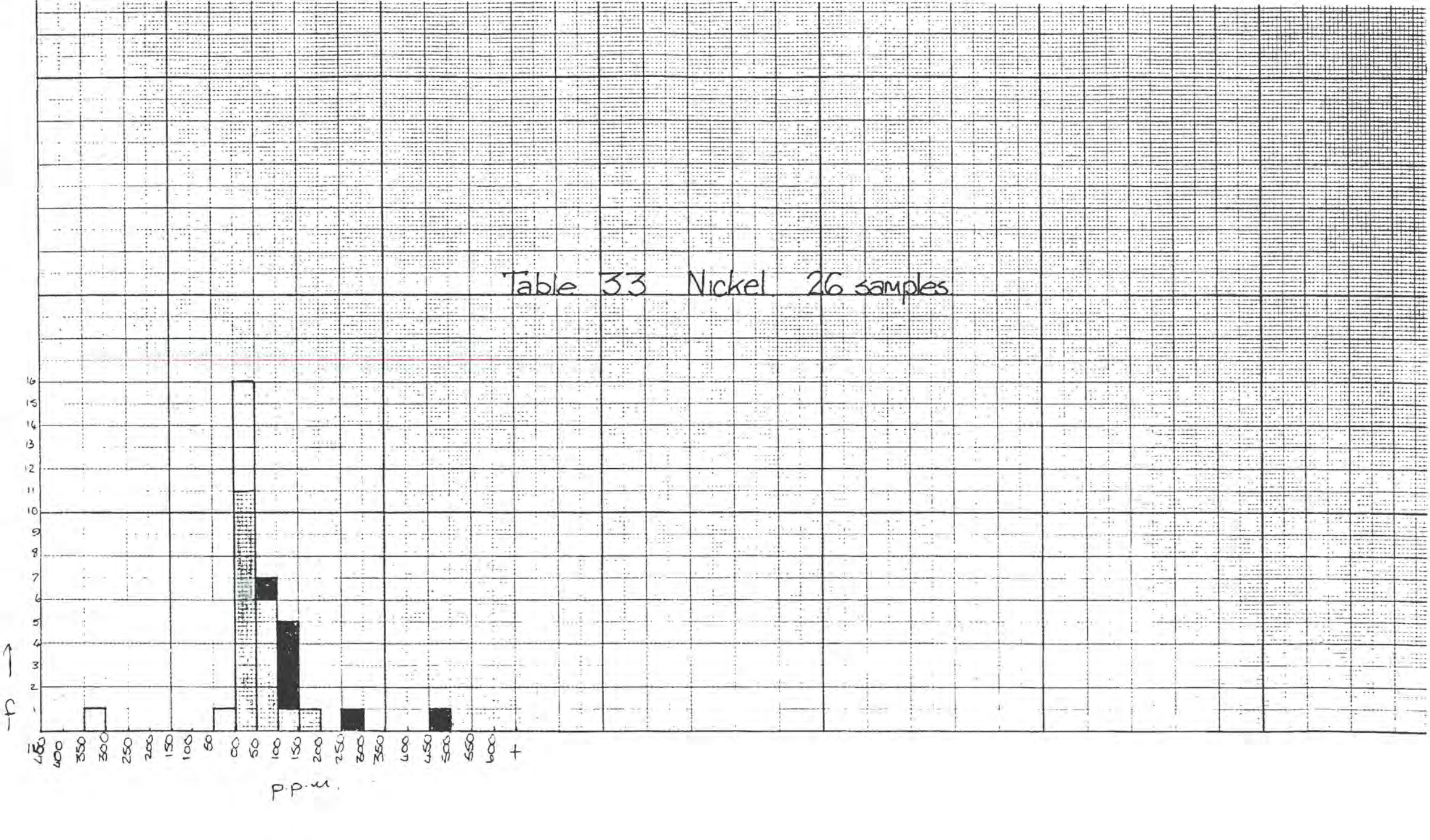


Table 33A Nickel

Samples: CW28
CF30

470

ppm

0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250

← N

Table 34 Copper 11 samples.

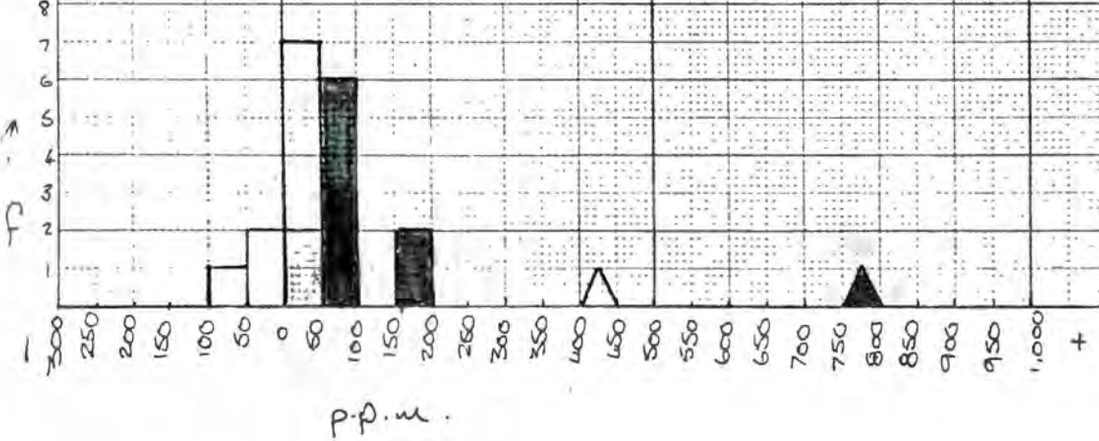


Table 34A Copper

samples: CW29
CF 11

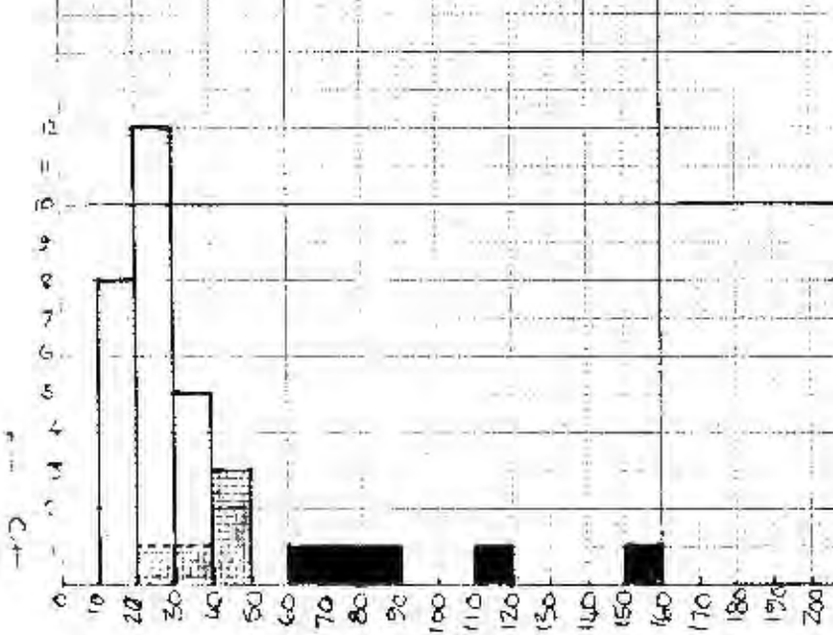


Table 35 Zinc. 12 samples.

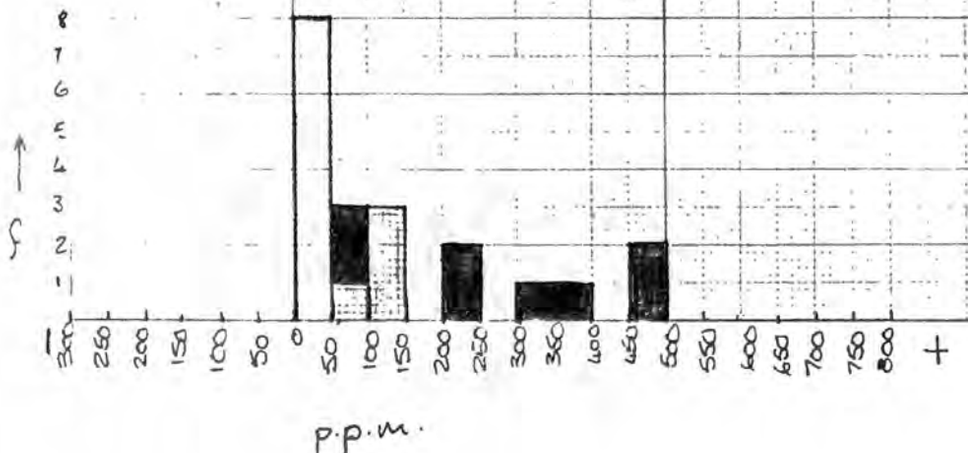


Table 35A Zinc

samples: CW 29
CF 17

1,131

291

407

393

531

p.p.m.

Table 36 Aluminium. 36 samples

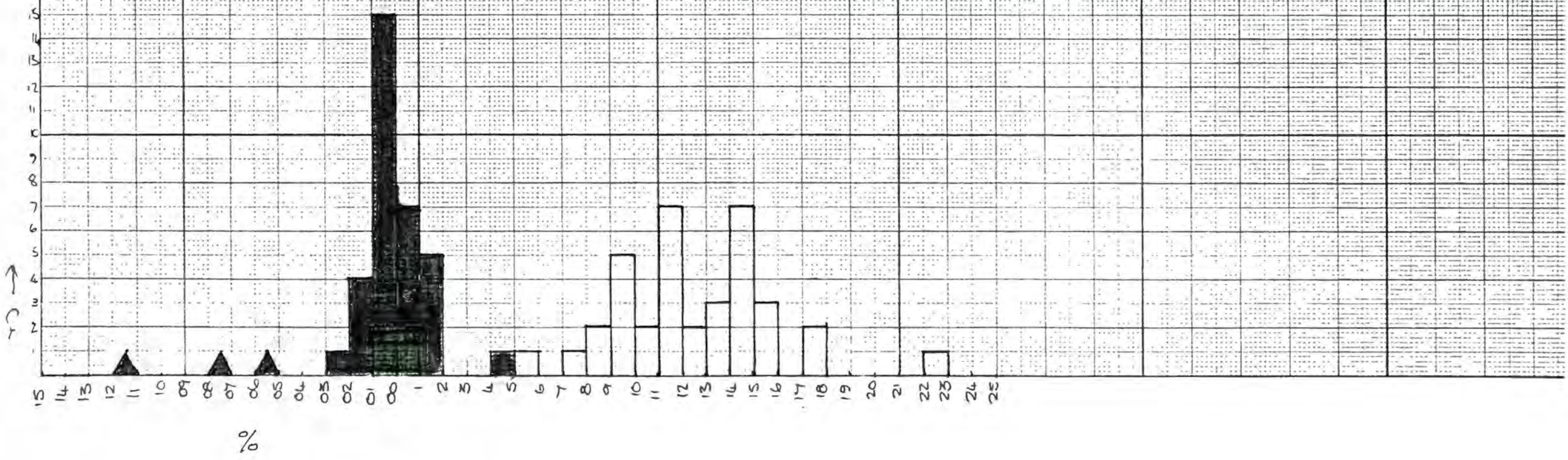


Table 36 A Aluminium.

Samples: CW/CF 36.

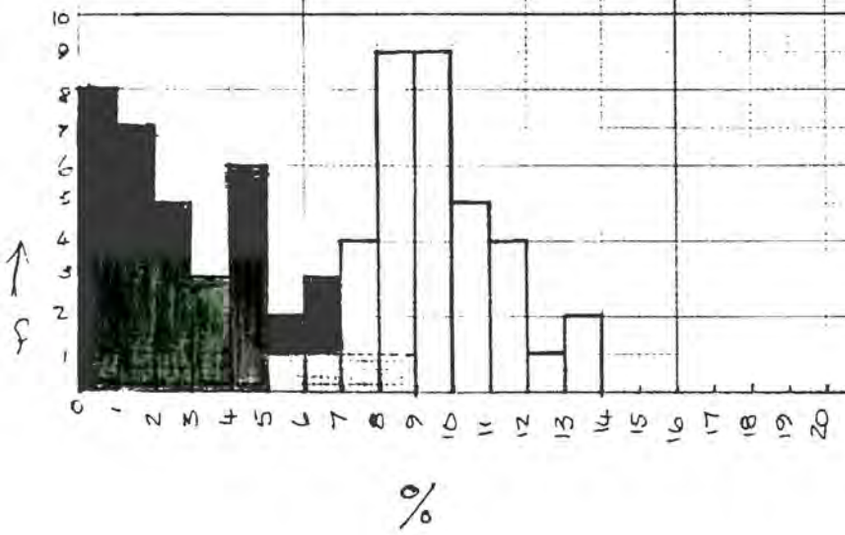


Table 37 Lead 12 samples.

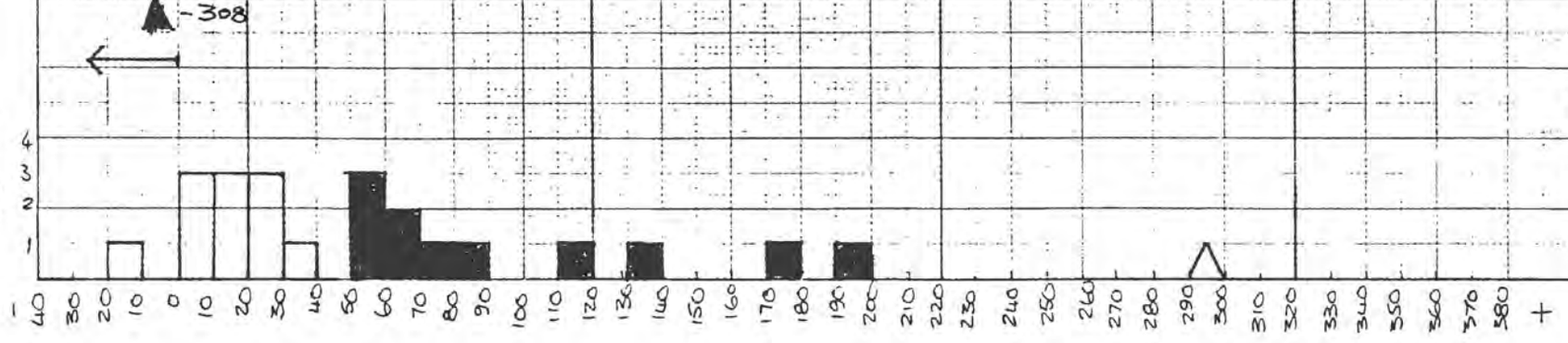
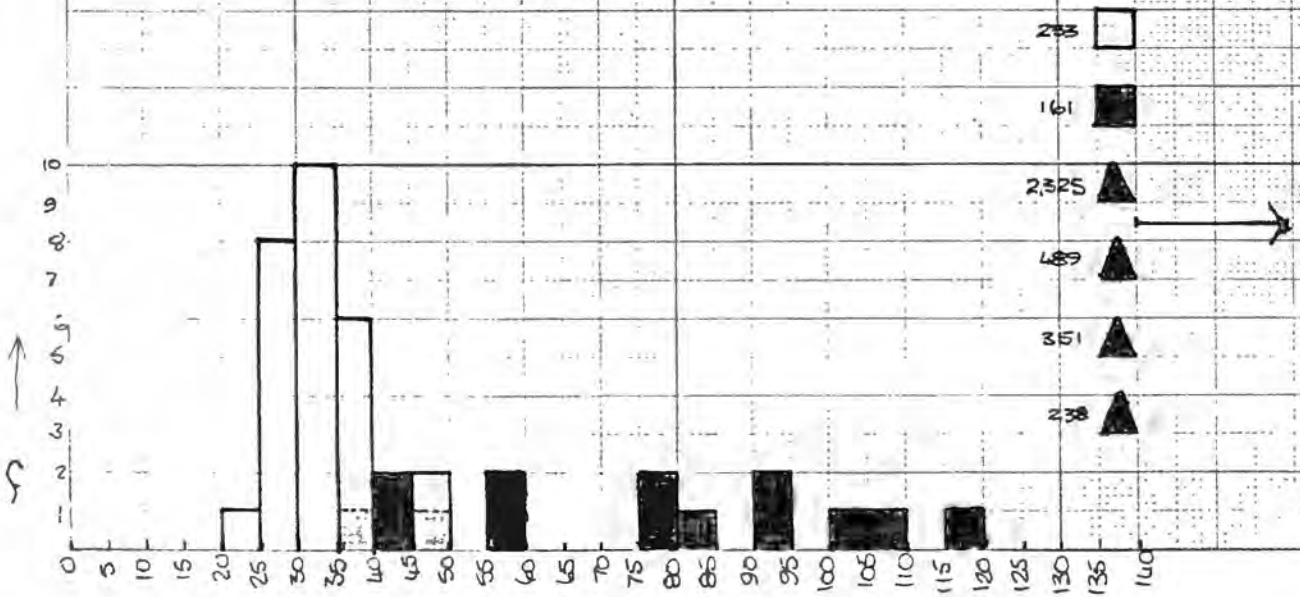


Table 37A Lead

samples: CW28
CF 19



Summary of Alkali Metals.

Li, Na, K are poorly concentrated. Rb, and probably Cs, are considerably concentrated with respect to the lighter alkali metals. It may be significant that this trend is in line with the residence times of this group. i.e. Rb and Cs are known to be removed from sea water faster than the other alkali metals, and it may be that organic matter plays a principal role in this removal. These times, from Riley and Skirrow, /25/ are given as:-

Li	2.0×10^7	i.e.	20,000,000	years
Na	2.6×10^8	i.e.	260,000,000	"
K	1.1×10^7	i.e.	11,000,000	"
Rb	2.7×10^5	i.e.	270,000	"
Cs	4.0×10^4	i.e.	40,000	"

Mg. See Table 6, 26, 26A, 39.
Mg is not concentrated in the organic fraction. The Black and White groups are separated and PER lies between -10 and +20.

Ca. See Table 7, 27, 27A, 40.
Ca is significantly concentrated when compared to Mg. The proportion of grey is high, although Black lies to the left of White. PER lies mainly from -10 to +40.

Sr. See Tables 8, 28, 28A, 40.
The Black-White distribution indicates that Sr, like Mg, is less concentrated than Ca. But the Sr PER values (-10 to +30) are more like those of Ca. It would have been very interesting to see the results for Barium, but no spectral lamp was available. According to Katchenkov /24/, Ba plays little part in the biochemistry of organisms, but is precipitated from solution by sulphur compounds, which are often related to decaying organic matter. Hence, indirectly, a relationship may exist between Ba and organic matter.

Summary of Alkaline Earths.

Residence times /25/ are:-

Mg	4.5×10^7	i.e.	45,000,000	years
Ca	8.0×10^6	i.e.	8,000,000	"
Sr	1.9×10^7	i.e.	19,000,000	"
Ba	8.4×10^4	i.e.	84,000	"

The results are in line with these times. One might predict high concentrations of Ba from its residence time.

Cr. See Tables 9, 29, 29A, 40.
Chromium is concentrated in the organic fraction, but not to a high degree. Black and White have considerable overlap, but most of the Cr is inorganic. PER lies between -10 and +30. Residence time is 350 years /25/.

Mo. See Table 10.
Mo was undetectable in all samples, mainly due to an ageing spectral lamp.

Mn. See Tables 11, 30, 30A, 41.
Mn is not significantly concentrated. PER lies between -10 to +20. Residence time is 1,400 years, but the removal of this metal is mainly in the form of Mn nodules./25/

Fe. See Tables 12, 31, 31A, 41.
Fe is not Concentrated in the organic fraction. PER lies between -10 and +20. Residence time is short (140 years /25/) probably because of the formation of Mn-Fe or Fe nodules.

Co. See Tables 13, 32, 32A, 41.
Cobalt is noticeably concentrated in the organic fraction, which usually has an equal or greater concentration of the metal than the inorganic fraction.

PER is variable, lying mainly between +10 and +80. Residence time is 18,000 years. /25/

Ni. See Tables 14, 33, 33A, 42.
Ni is concentrated. The organic fraction generally has similar or higher Ni values compared with the inorganic fraction. PER varies from about 0 to +70. Residence time is 18,000 years. /25/

Cu. See Tables 15, 34, 34A, 42.
The number of copper samples is low, because many were contaminated as described previously. It is clear, however, that Cu is considerably concentrated. PER is apparently very variable. Residence time is 50,000 years. /25/

Ag. See Table 16.
Ag was detectable in only one sample. No whole rock values were available.

Au. See Table 17.
Gold was detected in many samples, usually in amounts less than 30 p.p.m. No whole rock values were available and since these samples were not representative of average shales /1/, I decline to speculate further. Residence time is 560,000 years. /25/.

Zn. See Tables 18, 35, 35A, 42.
The number of Zn samples has been reduced by contamination. Even so, it appears to be concentrated but not to the extent that copper is. PER is widely variable. Residence time is 180,000 years. /25/

Al. See Tables 19, 36, 36A, 43.
Of the twenty elements studied, Aluminium shows the weakest correlation with organic matter. Black and White are strongly separated and PER is restricted to the range -10 to +10. Residence time is only 100 years, /46/. but this low value is misleading because most of the Al enters the oceans in solid mineral phases and rapidly settles out.

Pb. See Tables 20, 37, 37A, 43.
Like Cu and Zn, some Pb samples were disregarded because of contamination. Pb shows one of the strongest concentrations in the organic fraction. Black values lie well to the right of White and PER lies in the range +30 to +90. Residence time is 2,000 years. /25/.

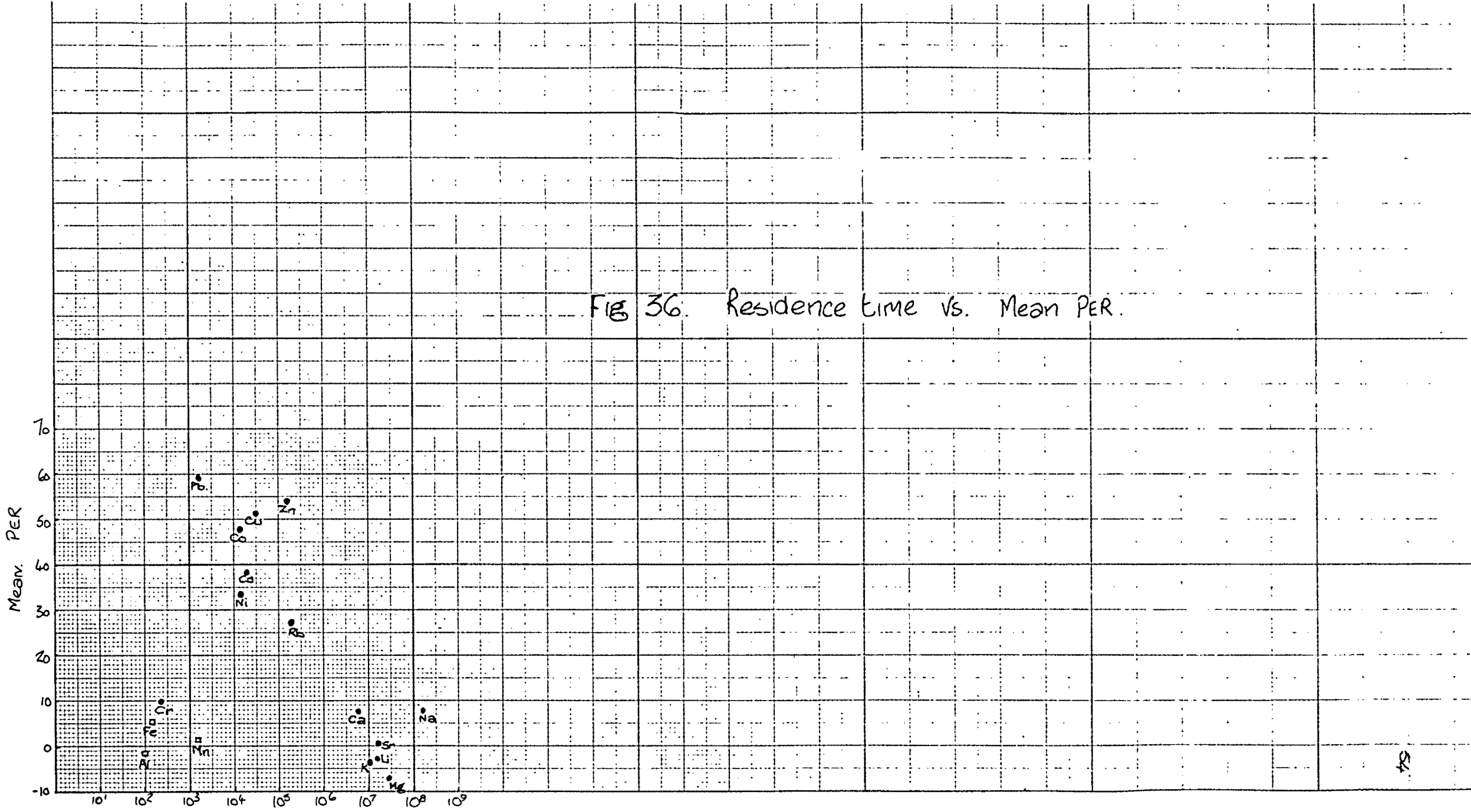
In the above discussion of the relative concentration of the individual elements in the organic fraction, I have included the residence times, in the ocean, of these elements. I showed that, for the alkali and alkaline earth metals, a rough inverse relationship exists between the concentration in the organic fraction and the residence time of the element. (I realize that residence times apply to the ocean and that most of my samples are almost certainly lacustrian /1/. However, I would like to persue this line of thought further, because the results are interesting. The conclusions I draw from them must not be regarded as more than speculation.)

In Fig. 36, I have plotted the residence time of each element against the Mean PER (from Tables 1-20) for the element. I regard PER as the best measure of the organophilic tendency of the elements. The results indicate a good inverse relationship. i.e. as the residence time decreases, the tendency to concentrate in organic matter increases, as might be expected if it is assumed that organic matter is one of the major removers of trace elements from water.

Four elements plot discordantly: Cr, Mn, Fe and Al. They are apparently removed from sea water faster than might be expected from their affinity for organic matter, indicating that some non-organic process is at work. I have already mentioned that for Mn, Fe and Al, these non-organic processes are well known. (Hence these elements are marked with squares in Fig. 36, since they do not represent real deviations from the straight line trend.)

Cr presents a real anomaly, though. Since Cr is not appreciably concentrated in Fe-Mn nodules /25/ some other inorganic process of removal is indicated.

Fig 36. Residence time vs. Mean PER.



c) Element Correlation.

A summary of the results of the Pearson's and Kendall rank correlations is given in Table F. The following points are of note:

1) Even at the 1% level, the number of correlations is remarkably high.

2) Agreement between Pearson's and Kendall rank is poor.

3) Good negative correlations are few.

4) Cu-Zn-Pb correlations show only when the results from contaminated samples are included. Therefore I have selected only those correlations which are consistent in each of the four groups - Cw, Cf, Co and Ci (See Tables 1-20 for explanation) and given them relative weight of 1 for very high consistency and 2 for good consistency. The numerical value of the correlation coefficient is not taken into consideration because of the variations mentioned above.

5) Agreement between overlapping groups (e.g. CI compared with CIS) is fair to poor.

From Table F, the following can be deduced:

1) No consistent pattern emerges.

2) K and Rb are related in the whole rock and in the inorganic fraction as expected, but not in the organic fraction, indicating odd behaviour of Rb in the organic matter compared to K.

3) In fact nothing is consistently related in the organic fraction.

4) Only two good negative correlations appear: K-Al and Mg-Al.

5) Five relationships seem to hold in all of Cw, Ci and Cf: Mg-Fe, Mn-Fe, Co-Ni, Na-K, K-Rb. There does not seem to be anything startling about these correlations.

TABLE F

SUMMARY OF CONSISTENT CORRELATIONS.

CW		CI		CF		CO	
1)	2)	1)	2)	1)	2)	1)	2)
K-Rb		K-Rb			K-Rb	None	
	K-Mg						
	Rb-Cs						
	Mg-Mn			Mg-Mn			
Mg-Fe		Mg-Fe		Mg-Fe			
	Cr-Ni						
Mn-Fe		Mn-Fe		Mn-Fe			
Co-Ni		Co-Ni		Co-Ni			
	Co-Zn						
	Ni-Al						
	Cu-Pb						
	Na-K		Na-K	Na-K			
	Na-Rb						
					Na-Al		
			[K-Al]				
			Mg-Zn				
			[Mg-Al]				
		Cr-Al					
			Fe-Zn				

1) Stronger Consistency

2) Weaker Consistency.

Negative correlations are marked with a block.

d) Metal Content versus PLOW.

Cw vs. Whole Rock PLOW. Figs 2-18

In the introduction, I said that it had been suggested that a direct relationship might exist between the concentration of some heavy metals and the PLOW on ignition of many samples. It came as a surprise, when I plotted these values for the elements I studied, to find that the only one which had a positive slope was Li, which should, in any case, have had a negative slope if this relationship held.

The results, which are my subjective interpretation of the graphs, are as follows. They are compared with results which Tables 1-20. led me to expect. The agreement is poor.

	Actual	Expected
Strongly defined Positive slope	None	Rb, Cs, Co, Ni, Pb, Zn, Cu
Weakly defined Positive slope	Li.	Ca, Cr.
Indeterminate	Cr, Mn, Ni, Cu, al, Pb.	Sr.
Weakly defined Negative slope	Cs, Fe, Co	Mn, Fe.
Strongly defined Negative slope	Na, K, Rb, Mg Ca, Sr, Zn	Li, Na, K Mg, Al.

This is peculiar, yet the analytical results show that some of the elements are concentrated by the organic fraction. The only explanations I can think of are the following:

1) There are not enough points to demonstrate the true trend.

2) As the proportion of metal rich organic material in the rock increases, the metal content of the inorganic fraction decreases.

Suppose, for example, that you have a marine environment (or even a lagoon or lacustrian environment) in which organic matter and clay minerals are forming or settling through a dilute solution of trace elements to collect as a shale. The bottom is stagnant and most of the organometallic absorption takes place from interstitial water which does not circulate readily. The clays and organic matter would compete for the absorption of trace elements and the organic matter would probably be more efficient, so that as the proportion of organic matter increases, the amount of Cu, Zn, Pb etc left for incorporation in the clay decreases.

3) The PLOW is not a reliable indicator of the percentage organic matter in the samples. They have been corrected for CO_2 loss, and since H_2O loss is negligible, it is difficult to imagine what else could be lost at 720°C that could cause serious error. According to Francis /4/ inorganic matter associated with kerogen or coal undergoes the following changes on ignition:

1) H_2O loss, mainly from clays.
2) CO_2 loss, mainly from carbonates.
3) $FeS \longrightarrow FeO + SO_2$.
4) Sulphur oxides + $CaO \longrightarrow CaSO_4$.
5) Loss of volatile chlorides.

It seems, then, that PLOW is probably a fairly accurate measure of organic content.

4) The metals are associated with some particular subfraction of the organic fraction, which in turn is unrelated to the total organic fraction. I regard this as the most likely explanation, but have no idea of the nature of the substance or substances in this subfraction.

Cf vs. Fraction PLOW. Figs 19-35.

In these figures, the PLOW for the fraction is plotted against Cf, the element concentration in the fraction.

If we group the graphs as in the section above, we find the following:

	Actual	Expected.
Strongly defined Positive slope	None	Pb, Cu, Zn, Rb Cs, Co, Ni.
Weakly defined Positive slope	None	Ca, Cr, Au?
Indeterminate	Cs, Ca, Sr, Cr, Ni, Zn, Pb	Sr.
Weakly defined Negative slope	Li, Rb, Co	Mn, Fe
Strongly defined Negative slope	Na, K, Mg, Mn Fe, Cu, Au, Al	Li, Na, K Mg, Al

Again, the agreement between "Actual" and "Expected" is very poor, expecially for positive slopes. The agreement between Cw-PLOW and Cf-PLOW is not good. It seems that the elements concentrated by the organic fraction (Rb, Cs, Ca, Cr, Co, Ni, Cu, Zn, Pb) have a tendency to give indeterminate plots (four out of eight for Cw, six out of eight for Cf).

3.7 A DISCUSSION OF THE GEOLOGICAL ROLE OF CAUSTOBIOLITHS.

Before drawing any conclusions from my results, I would like to spend some time discussing the role played by organic matter in the geochemical cycle.

The inter-action of organic matter and the elements in the sedimentary cycles which produce caustobioliths is insufficiently understood. The elements entering any basin of deposition (marine, terrestrial, peat bog etc.) may be derived from the weathering of igneous, metamorphic or older sedimentary rocks, or from organic sources. /24/. These elements may be:

1) in solution

2) associated with terrigenous material. The importance of the composition of the mineral detritus, in relation to the organic matter, is not to be underrated. It can seriously influence the trace element content of the organic fraction by various chemical reactions e.g. ion exchange or acid attack. For example, Wedepohl /26/ demonstrates that a large mass of trace elements (Cu, Zn, V, Pb) enters the sedimentary environment absorbed to ferric oxide, which in turn coats larger mineral grains such as quartz. Organic matter reduces the oxide, and releases the trace metals, which may be promptly secured by H_2S or organic compounds present in the reducing environment. Furthermore, a high concentration of a particular element in the mineral fraction may swamp the concentration in the organic fraction when an attempt is made to correlate the whole rock value for that element and the amount of organic matter. /26/.

3) Present in organisms. /24/

According to Katchenkov /24/, certain elements (e.g. Ba, V, Cr, Mn, Ni, Co, Cu, Zr, Be) are either dominantly in the terrigenous minerals, or are rapidly precipitated by one means or another because they are inherently "insoluble". Other elements like Sr, Na and K are "soluble" and have large residence times /25/ and stay in solution until removed by an unusual and specific mechanism. e.g. Sr is chemically precipitated in lagoons /24/ or removed biogenetically, associated with

Ca in calcereous tests. /24/ (It should be noted that there is evidence /28/ for the association of Sr with soft tissue also) On the other hand, Na is removed mainly in salt deposits.

Although most of the discussion in this work concerns the immobilization of ions by organic matter, it should not be forgotten that organic matter affects geochemical distributions in the reverse manner, too. For example, organic molecules are important mobilizers (especially during weathering) of metals like Fe, Al, Ti, V, U and other heavy metals /6/, which would otherwise be very insoluble.

What becomes of these "insoluble" elements mentioned by Katchenkov? /24/. Below is a list of elements, given by Wedepohl /26/, whose concentration in a sediment is sensitive to the Eh in the sediment at the time of formation. These elements tend to be fixed by the reducing environment: V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Mo, Ag, Sb, Pb, U and Tl. A comparison of this list with that of Katchenkov shows that the heavy metals predominate in both groups.

I (and others /3, 4, 7, 8, 9, 24, 26, 28, 41/) think that it can be accepted that the distribution of many of these elements is strongly influenced by the presence or absence of organic matter. Fig R4, from Wedepohl /26/, shows the relationship between the elements Cr and Ni and the carbon content of samples from the Kupferschiefer.

It seems, then, that we can divide most metals into two broad groups according to their affinity to organic matter. We have the heavy metals which are "organophilic" and the lighter elements which are "organophobic" or "organo-apathetic". This classification is useful but must not be taken too far, as can be seen from Fig R7 (reproduced from Szalay /3/) which shows that practically all metals have some affinity for humic substances.

In a laboratory experiment, Ganguly /41/ showed that Zn, Mn and Co were absorbed by samples of marine coastal sediments 3 to 30 times better than if the organic matter of these sediments was first removed by H_2O_2. The alkalis and alkaline earths, Cs, K, Ca and Sr were absorbed almost equally by both treated and untreated samples. There is, however, little doubt that the lighter metals are capable of forming organic complexes (Fig R7). Ganguly infers from this that the alkalis and alkaline earths are held in exchangeable cationic forms and that metals like Zn, Mn, Cu and Co are held in less exchangeable cationic, or noncationic forms.

The foregoing discussion does not mean that the distribution of these elements is not influenced by other factors. It has been shown, for example, that illite absorbs Cu ions strongly under certain conditions /26/. Also, the presence of organic matter does not guarentee a concentration of all heavy metals. For example, Wedepohl /26/ found that in 30% of his Kupferschiefer samples, the Zn content was below the value for an average shale (100 p.p.m.). Furthermore, in the same study, a direct relationship was found between Mn and the carbonate content of the samples rather than the more ubiquitous organic content.

<u>How does the organic matter actually affect or interact with these metals</u>? For purposes of discussion, assume that a sediment is accumulating slowly under quiet, reducing conditions. The detrital and organic matter can be supplemented by:

1) Precipitation, which is influenced by pH, Eh, the availability of gases like H_2S and the concentration of metal ions in solution. /29, 34/. Neglia et al /44, 45/ found a fair to good correlation between organic matter and pyrite in the black shales of the basins they studied. In addition, they found /45/ that the reducing environment favours the formation of mixed layer clays and, since clays are also important sorbtion agents /26/, the organic matter has a further indirect control over trace element fixation.

Fig R7.

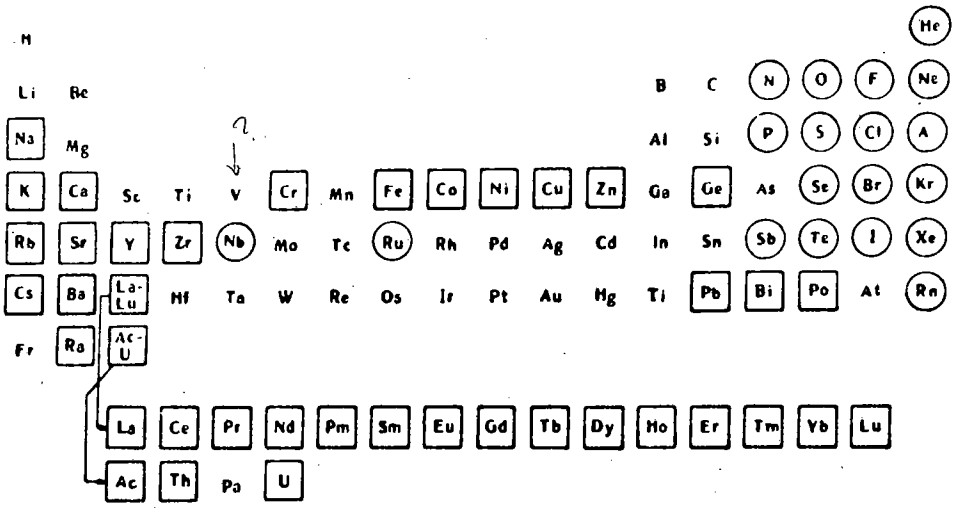


FIGURE 4. Arrangement of elements in the periodic system indicating concentration by humic acids. Elements in squares are sorbed, those in circles are not, while the remaining elements were not investigated.

Fig R8.

TABLE III

EFFECTIVE IONIC RADII AND RELATIVE SURFACE POTENTIAL OF IONS OF VARIOUS ELEMENTS IN DILUTE AQUEOUS SOLUTION

Ions	"Effective radius"	Relative surface potential
Rb^+, Cs^+, Ag^+	1·25 Å	0·64
K^+	1·5 Å	0·44
Na^+	2·0 Å	0·25
Pb^{++}	2·25 Å	0·395
Sr^{++}, Ba^{++}	2·5 Å	0·32
Ca^{++}, Zn^{++}, Sn^{++}	3·0 Å	0·22
Mn^{++}, Fe^{++}, Ni^{++}, Co^{++}		
Mg^{++}	4·0 Å	0·125
Li^+	3·0 Å	0·11

2) Sorbtion of ions, complexes or organic compounds from the water onto the sedimentary particles. The main sorbtion agents are clays, hydroxides (notably of Al, Fe and Mn) and organic matter. /29, 34/. The factors governing the sorbtion process are not well known /29/ but are undoubtedly complicated. Nicholls /29/ points out the difficulties of trying to use theoretically determined atomic properties like ionic size to expose trends in the distribution of elements in organic matter. For example, the small ion Li^+ more than doubles its volume in water by surrounding itself with a sheath of electrically attracted H_2O dipoles. Fig. R8, from Nicholls' paper /29/, shows the effective radius of several cations in dilute solution together with their relative surface potentials (RSP = charge/area). According to him, elements with RSP's greater than 0.3 or less than 0.2 are strongly sorbed by clays, while those in the range 0.2 to 0.25 are sorbed strongly by organic matter.

This observation is empirical and the reasons can only be guessed at.

Despite the shortcomings of a theoretical approach, it is possible to find relationships between the ionic or atomic properties of elements which behave similarly towards organic matter. Fig. R9, from Mason /30/ shows a clear relationship between the ionic radius, ionic charge and the concentration ratio in plants (relative to the average rock) of the elements plotted. Elements of low ionic potential (giving soluble cations) and high ionic potential (giving soluble anions) are readily assimilated. The intermediate elements, forming insoluble hydrolystates are not concentrated.

Meanwhile, back in our sediment, the transfer of metals is being complicated by the release, through decay, of metals held by organic matter already in the sediment. The fate of trace elements released by the decay of the soft parts of organisms is poorly known /29/. However, since the metals are released into an environment of low Eh, restricted circulation, high concentration of H_2S and where many new organic molecules are forming,

Fig R9

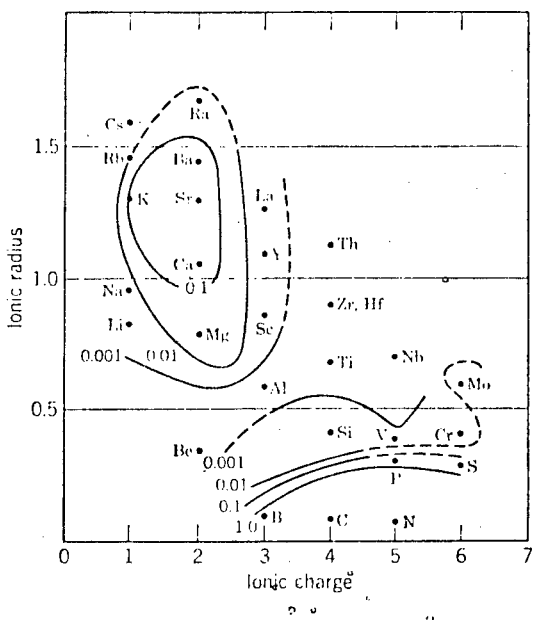


Figure 9.2 Concentration ratio of elements in terrestrial plants and in the crust, in relation to ionic potential. (Hutchinson, 1943, p. 337)

it is probable that much of this trace metal is retained within the sediment in some new combination.

In general, then, free trace element ions or complexes from both internal and external sources are subject to the following modes of fixation by organic material. /26/

1) Decrease in solubility and precipitation after reduction eg V^{5+} V^{3+}, U^{6+} U^{4+}.

2) Precipitation of sulphides e.g. Cu, Ag, Pb, Zn and Cd.

3) Sorbtion by organic debris (e.g. Ag, Cu, Zn and Pb).

Of course, all these reactions are subject to the availability of the element in the water. /29/.

While I have emphasized those processes which eventually fix the metals in the sediment, the important organometallic reactions which take place in the free water above the sediment must not be overlooked. Many organometallic compounds have been identified in sea water /19/ and it may well be that these organometallic molecules are more readily absorbed by the sediment than free ions would be. Fukai /40/ has demonstrated that the rate of metal exchange between free floating organically bound and ionic forms is slow.

Curtis /28/ gives the following rather satisfying model of the incorporation of trace elements into the sediments. The organic matter of sediments is either present in detrital grains, or is more commonly absorbed onto the surface of clay particles. I have included elsewhere in this thesis Curtis' evidence for the existence of this film, with a reproduction of his micrographs. (Plate 1). Experiments have shown that clays quickly and irreversibly absorb organic molecules from solution to form thick films. For example, alanine is absorbed onto montmorillonite in a layer 65 molecules thick, demonstrating that a given amount of clay can fix 3 or 4 times its own mass of organic matter. Furthermore, factors like pH, salinity and temperature have little effect on this process. /28, 29/.

Plate 1.

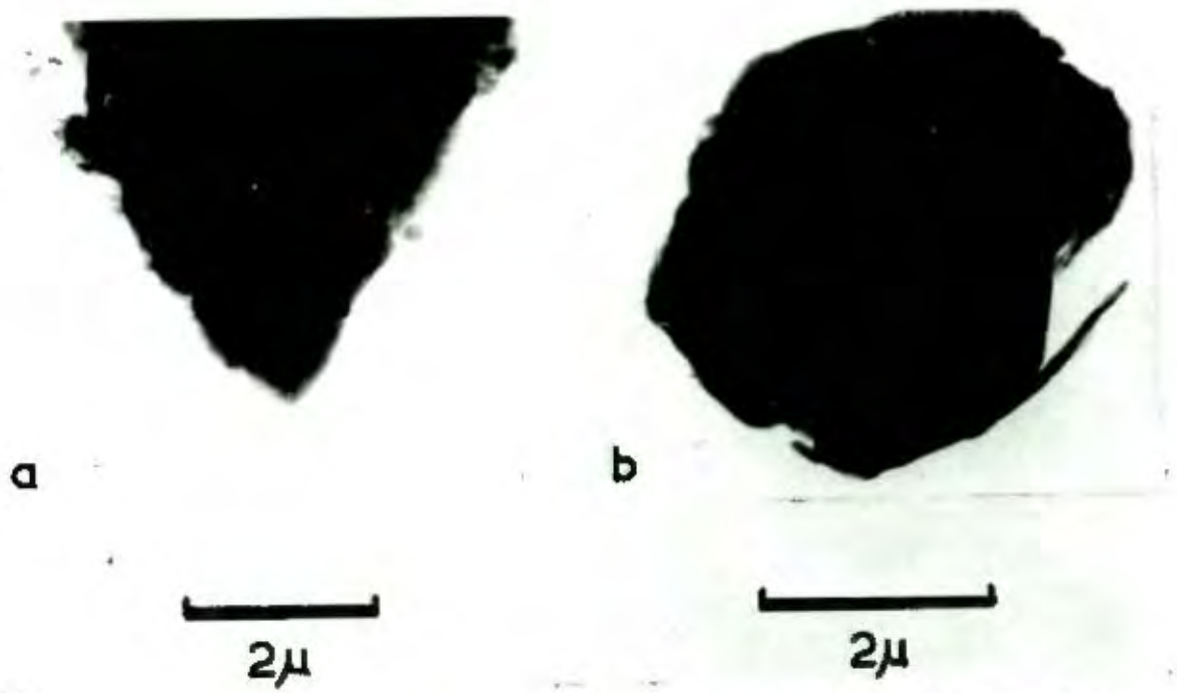


FIGURE 4.—Electron micrographs of clay particles: (a) untreated; (b) oxidized.

Since the surface area of the clays is vastly in excess of that of the detrital fraction, the organic coated clays tend to dominate the absorption characteristics of the sediment. To an approaching ion or molecule, which must react with the surface of a sedimentary particle and not its interior, the sediment must appear to be largely organic. Now these approaching particles may be:

a) Organic molecules in solution.
b) Organometallic complexes and complex organic ions, mainly of the transition metals.
c) Simple or aqueous inorganic ions.

As we have seen, the clay will attract particles of type a). The "clay - a" combination (i.e. organic coated clay) will attract b) molecules i.e. organometallics. Hence the concentration of elements like Cu, Mo, Co and Ni which form stable organometallic complexes.

The ions of group c) do not like organic matter. They can be divided into two types, ci and cii. Ions of type ci do not like inorganic matter either and are not attracted to the inorganic part of the sediment e.g. quartz or uncoated clay. Therefore, if an element of this type (e.g. Na) is concentrated in the sediment, some other mechanism must be sought. Ions of type cii are attracted to the inorganic fraction, and will absorb onto those mineral surfaces which are not totally blocked off by organic films. This explains the inverse relationship between certain elements (notably boron) and organic matter in sediments. Boron has a strong affinity for illite /28/ but when organic matter is present with the illite, its concentration is usually low.

Since type b) complexes are generally less sensitive to factors like Eh and pH than complexes of type c), it follows that the "clay - a - b" association occurs more regularly than "clay - a - c" association. For example, we are almost sure to find Cu concentrated in a caustobiolith, but an alkali like Rb may only be concentrated in a narrow pH or Eh range and is therefore rarely concentrated in caustobioliths. This regular occurence in caustobioliths of the transition metals,

and the irregular occurence of most of the other metals is frequently noticed.

Curtis lists the following elements as being of type b), i.e. are directly related to the organic fraction: V, Cr, Mn, Ni, Co, Cu, Mo and U. Boron has been shown to be inversely related, while metals like Sr and Ba seem to be indifferent.

Curtis points out that this argument does not hold in sediments with a high proportion of detrital matter.

In general, then, and especially in the presence of H_2S, the reducing sapropelic environment becomes a "sink" for most of the heavy metals like Cu, Co, Ni etc. However, the chemistry of the situation is complex and in some environments /26/ which are not well studied, some metals (notably Fe and Mn) may be actively lost to the water and carried away despite the reducing conditions.

What proportion of the Trace Metals in the organic fraction of a shale was present in the organism before death?

This is an unresolved problem, and at present the best that the experts can say is that it is highly variable and dependant on little known factors /3, 4, 37/.

For example, in the Kupferschiefer /26/, the concentration of some trace metals is so high that it becomes obvious that enrichment from the solution must have occured. Of course, it is debatable whether the metal in solution came from an inorganic or organic source. Also, the nature of the original organisms seldom determines the final distribution and concentration of trace elements in caustobioliths /29/, indicating the important role of posthumous sorbtion processes. On the other hand, biochemically selective absorption by coal-forming land plants /30/ of various elements is the best way of explaining the following features of most coal ashes /30/.

1) The elements present differ widely in geochemical behaviour.

2) Both chalcophile and lithophile elements are present.

3) Ionic or atomic radii seem to be unimportant.

A very recent study by Calvert and Price /37/ has shown that in young unconsolidated shelf sediments, off South West Africa, concentrations of the metals Cu, Ni, Pb and Zn are strongly related to the organic content, and that this concentration is due principally to the accumulation of these metals by plankton during their life cycle. (This is a region of upwelling and high plankton activity). Figs. R10 and R11 are reproduced from their paper. They show clearly the correlation between the distribution on the shelf of organic rich sediment and the distribution of Cu, Zn, Ni and Pb.

They found the following values in the sediments:

Cu	18-129	p.p.m.
Ni	35-455	"
Pb	3- 32	"
Zn	18-337	"

In addition, Cu and Ni were strongly correlated to each other. They noted too, that the Cu and Pb values of the S.W. African sediment were much like those of similar sediments elsewhere, but that the Ni and Zn were somewhat higher in the former.

They found that plankton are powerfull metal extracters. The most abundant diatom in the Benguella current, CHAETOCERAS CURVISETUS was found to have the following amounts of metal (dry weight, in p.p.m.)

Cu	300 - 6000
Ni	60 - 90
Pb	1200 - 1800
Zn	6000 - 9000

Chaetoceras is rapidly decomposed and its trace elements would be released into an environment of low pH and high H_2S content, and would probably be largely immobilized in the sediment. The authors believe that these metals "are intimately associated with the organic fraction of the sediment" but they emphasize that in most deposits we know little about the relative contributors from biogenetic, terrigenous and authigenic sources.

Fig R10

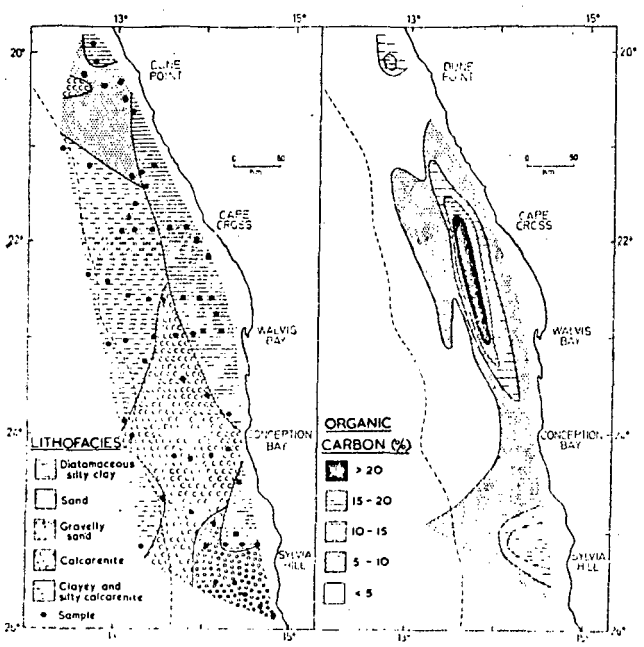


Fig. 1. Distribution of lithofacies and organic carbon in South West African continental shelf sediments. The dashed line, the 500 m isobath, marks the approximate boundary of the shelf. Organic carbon values are given on a salt-free basis.

Table 2. MAXIMUM CONCENTRATIONS (P.P.M.) OF MINOR METALS IN SOUTH WEST AFRICAN SHELF SEDIMENTS TOGETHER WITH THE ORGANIC MATTER AND TERRIGENOUS CONTENTS (PER CENT) OF THE SAME SAMPLES

	Metal concentration	Organic matter*	Terrigenous constituents†
Cu	129	39·1	6·0
Ni	455	36·7	6·9
Pb	32	18·7	18·2
Zn	337	31·1	33·8

* Organic carbon ×1·7.
† Difference between the sum of $CaCO_3$, organic matter and opal contents and 100 per cent.

Fig R11

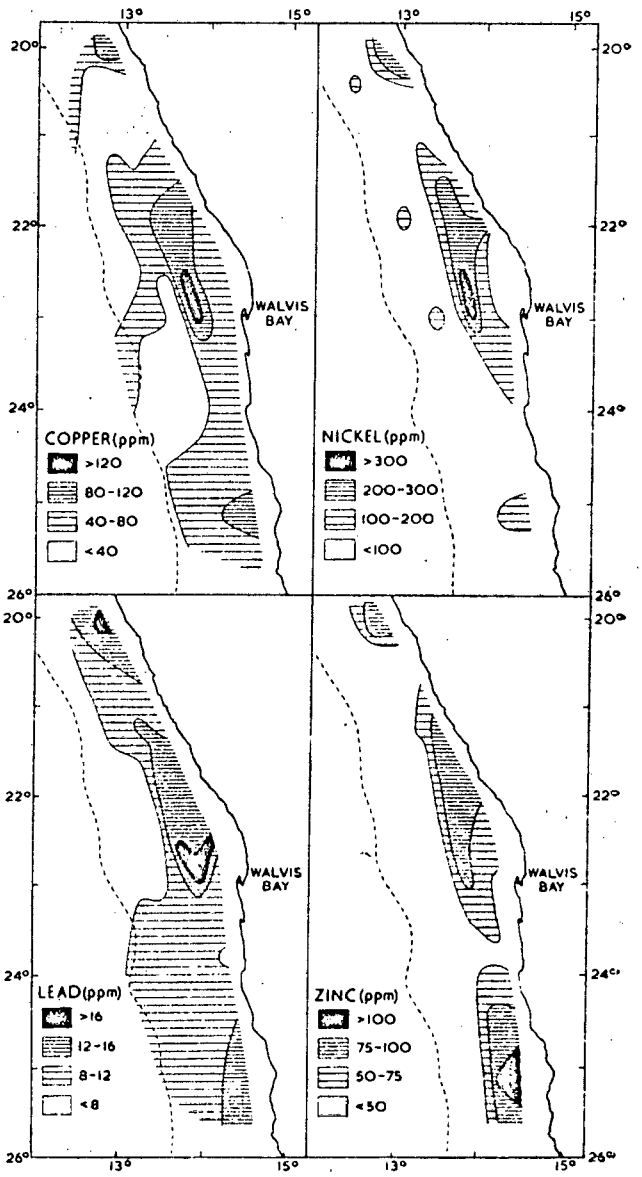


Fig. 2. Distribution of Cu, Ni, Pb and Zn in South West African continental shelf sediments. All values on a salt-free basis.

A wide literature exists, /6, 23, 37, 38/ on the role and content of metals in many organisms. In many cases the relative concentration is dramatic. /37, 38/ Two types of bio-metal are distinguished:-

1) Those used in the life processes. For example, Mg occurs in chlorophyl and Fe in Haemin, while V and Cu are essential in the "blood" of some organisms /30/.

2) Those which are not used in the life processes, and just happen to be in the organism because they are present in the surroundings. For example, the locoweed in the U.S.A. concentrates Selenium in rough proportion to the content of this metal in the soil, and is used in geochemical prospecting for this element /30/.

Organisms take up elements of equal crustal abundance in very unequal amounts /30/, these amounts being dictated mainly by the needs of the life process. In a study of the metal content of various species, it should be remembered that micro-organisms are quantitatively more important than macro-organisms in trace element organic geochemistry, because of their vast numbers. The concentration of trace elements in plankton has already been mentioned. As a further example, Day /38/ states that Spirogyra growing in water which contained a total of 16 p.p.m of heavy metals had in them (dry weight)

2900 p.p.m Zn
6600 " Pb
920 " Cu.

Most of the Cu of terrestrial lakes is locked up in plankton /38/.

Projects are at present in progress /41/ to follow the path of elements in the biogeochemical cycles by means of radiotraces, and much useful information from this source should be available soon.

A summary of the main biological features of the individual elements is given elsewhere in this work. However, the reader may find Figs R12, R13, R14 and R15 (from Mason /30/) useful as an indication of the magnitude of the concentration of some elements in a few organisms.

Fig R12

*Table 9.1. Distribution of Elements as Percentage Body Weight of Organisms**

Invariable			Variable		
Primary 60–1	Secondary 1–0.05	Micro-constituents <0.05	Secondary	Micro-constituents	Contaminants
H	Na	B	Ti	Li	He
C	Mg	Fe	V	Be	A
N	S	Si	Br	Al	Se
O	Cl	Mn		Cr	Au
P	K	Cu		F	Hg
	Ca	I		Ni	Bi
		Co		Ge	Tl
		Mo		As	
		Zn		Rb	
				Sr	
				Ag	
				Cd	
				Sn	
				Cs	
				Ba	
				Pb	
				Ra	

* Webb and Fearon, 1937, with additions. Webb and Fearon remark that for some of the elements the number of organisms analyzed by reliable methods is insufficient to enable to one to decide whether an element is strictly variable or invariable, and, furthermore, that the quantitative classification, though convenient, is necessarily arbitrary.

Fig R13

Table 9.2. The Relative Amounts of Different Elements in Igneous Rocks and in Organisms

	(1) Percentage in Igneous Rocks	(2) Percentage in Living Terrestrial Plants	Ratio (2):(1)
Li	0.0065	0.00001	0.0015
Na	2.83	0.02	0.007
K	2.59	0.3	0.12
Rb	0.031	0.0002	0.0066
Mg	2.09	0.07	0.034
Ca	3.63	0.5	0.14
Sr	0.015	0.002	0.13
Ba	0.025	0.003	0.12
Rare earths	0.0148	0.00004	0.0027
Al	8.13	0.002	0.00025
Ti	0.64	0.0002	0.00032
Si	27.72	0.15	0.0055
B	0.0003	0.005	1.7
P	0.08	0.07	0.88
S	0.052	0.05	0.96
V	0.015	0.00002	0.0013
Mo	0.0015	0.00005	0.033

After Hutchinson, 1943.

76.

Fig 8 R14

H ≡																	He
Li =	*Be* =											B =	C ≡	N ≡	O ≡	*F* =	Ne
Na ≡	Mg ≡											*Al* =	Si =	P ≡	S =	Cl ≡	A
K ≡	Ca ≡	*Sc* =	*Ti* ≡	*V* ≡	*Cr* =	Mn =	Fe =	Co =	*Ni* =	Cu =	Zn =	*Ga* =	*Ge* =	*As* =	*Se* =	*Br* ≡	Kr
Rb =	*Sr* =	*Y* =	Zr	Nb	Mo =		Ru	Rh	Pd	*Ag* =	*Cd* =	In	*Sn* =	Sb	Te	I =	Xe
Cs =	*Ba* =	*La-Lu* =	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	*Pb* =	Bi			
	Ra =		Th		U												

Invariable { Primary (1–60%) ≡ ; Secondary (0.05–1%) = ; Microconstituents (<0.05%) – }

Variable { *Secondary* = ; *Microconstituents* – }

Figure 9.1 Elements classified according to their distribution as percentage body weight of organisms. (After Webb and Fearon, 1937, with some more recent data)

Fig R15

Table 9.3. Elementary Composition (Weight Per Cent) of Different Organisms

Calanus finmarchicus (a copepod)*			Alfalfa (lucerne)†			Man‡		
O	79.99		O	77.90		O	62.81	
H	10.21		C	11.34		C	19.37	
C	6.10	n. 10^{0}	H	8.72	n. 10^{0}	H	9.31	n. 10^{0}
N	1.52		N	8.25		N	5.14	
Cl	1.05					Ca	1.38	
Na	5.4	n. 10^{-1}	P	7.06	n. 10^{-1}	S	6.4	n. 10^{-1}
K	2.9		Ca	5.80		P	6.3	
S	1.4		K	1.70		Na	2.6	
P	1.3		S	1.037		K	2.2	
						Cl	1.8	
Ca	4	n. 10^{-2}	Mg	8.2	n. 10^{-2}	Mg	4	n. 10^{-2}
Mg	3		Cl	7.0				
Fe	7	n. 10^{-3}	Si	9.3	n. 10^{-3}	Fe	5	n. 10^{-3}
Si	7		Fe	2.7		Si	4	
B	1.5		Al	2.5		Zn	2.5	
Br	9	n. 10^{-4}	B	7.0	n. 10^{-4}	Rb§	9	n. 10^{-4}
I	2		Rb	4.6		Cu	4	
Cu	6		Mn	3.6		Sr	4	
			Zn	3.5		Br	2	
			Cu	2.5		Sn	2	
			F	1.5		Mn	1	
			Mo‖	1		I	1	
V	4	n. 10^{-5}	Ti	9	n. 10^{-5}	Al	5	n. 10^{-5}
Mo	2.4		Ni	5		Pb	5	
Ti	2		Br	5		Ba	3	
			Ti	4.6		Mo§	2	
			V	1.6		B	2	
Co	6	n. 10^{-6}	I	2.5	n. 10^{-6}	As	5	n. 10^{-6}
			Co	2		Co	4	
						Li§	3	
						V§	2.6	
						Ni	2.5	
						As, Sn, Pb, Sr, Ba	n. 10^{-n}	

* Vernadsky, *Z. Krist. Mineral. Petrog.*, Abt. B, *Mineral Petrog. Mitt.* **44**, 191, 1933.
† Water, 75.1%; org., 22.45%; ash, 2.45%; from Bertrand, 1950, p. 442.
‡ Water, 60%; org., 35.7%; ash, 4.3%; from Bertrand, 1950, p. 442.
§ Mean figure for mammals.
‖ Normally in plants, 3.10^{-5}.

No one seems to know much about the influence of percolating ground waters on the metal content of the organic matter./3, 4/ Wedepohl /26/ has a convincing argument against the large scale enrichment of heavy metals in the Kupferschiefer by ground water. On the other hand, U and other metals are known to be introduced into peat deposits by ground water./3/ Degens et al /17/ also stress the influence of circulating ground waters on the metal content of caustobioliths.

What are the similarities and differences between the trace element content of petroleum, coal, kerogen and other caustobioliths? Many similarities and differences do exist, but no one has adequately explained them. Petroleum is a better concentrator of trace elements than is coal /30/ or kerogen. The reason may lie in the mobile, bituminous nature of petroleum as opposed to the humic nature of coal, but this is unproved.

According to Zul'fugarly /33/, petroleum microelements differ from those of most humic caustobioliths. They have more regularities and are more often related to the country rock. This indicates that petroleum, because of its fluid nature, picks up trace elements from the country rock more readily than kerogen. However, the metal content of the parent organisms of petroleum is also important in determining the final trace element distribution. /33/. He gives, as an example of the trace elements found in petroleum, analyses of the ashes of many petroleum samples from the U.S.S.R./33/ The elements invariably present are: Na, Cu, Mg, Ca, Sr, Ba, Zn, Al, Ti, V, Cr, Mn, Fe, Co, Ni. Those frequently present are: K, Ag, Sn, Pb, Mo and the following occur sporadically: Li, Be, Cd and Ga. V and Ni and to some extent Cu are ubiquitous in the world's petroleums/33/. In many cases V_2O_5 + NiO + CuO comprises more than 75% of the petroleum ash which can be used as ore /33/. V and Ni are believed to aid the genesis of petroleum /33/.

On average, humic materials are much poorer than petroleum in V and Ni.

According to Francis /4/ 95% of the ash of the average coal consists of Al, Si, Fe and Ca. (Much of this is adventitious, i.e. present in minerals rather than inherent, i.e. present in the plant matter)/4/. The other 5% is mainly Mg, Na, K, Ti, Cl, Cs and P, while the most common trace metals are V, Sc, Ga and Ge. The elements which have been found to be associated with the organic structure of various coals are B, Sn, Ni, Cu Zn, Ti, V, Cr, Ge and Ga. /4/. Some of these may be present as porphyrins, since it has been established that porphyrins of V and other heavy metals exist in coal /4/. Fig. R16 from Francis /4/ lists the amounts of several elements in average coal ash and the earth's crust and also the relative enrichment of these metals in the coal ash. Fig. R17 from Mason /30/ shows similar parameters for coal ashes from New South Wales.

The main factors affecting the concentration of trace metals in coal seem to be:
1) The solubility of the metal, which determines how much the plant can take in.
2) Ground water absorption /4/.

There is a wide literature on the organometallics found in soils. /42/. These have many features in common with the organometallics of hard rock and the study of soil organometallics can undoubtedly advance the subject.

Manskaya and Drozdova /6/ summarize the factors which they regard as important in the control of the trace element concentration in various caustobioliths. These are:
1) The chemical composition of the organic material.
2) the properties of the element.
3) The conditions of reaction.
I would add to this the availability of the element.

What is the chemical nature of the naturally occuring organometallic compounds? Our present state of knowledge of this subject is fragmentary /30, 40/, especially in the case of the humic-metallic bonds which are difficult to characterize /6/.

Undoubtedly chelates are an important group/6/.

Fig R16

TABLE X.VI.

RARE ELEMENTS IN THE ASHES OF COAL (GRAM. PER TON) after Goldschmidt.

Element	Max.	Aver. of "rich" Ashes	Earth's Crust	Factor of Enrichment	
				Max.	Aver.
Boron	3,000	600	3	1,000	200
Germanium	11,000	500	7	1,600	70
Arsenic	8,000	500	5	1,600	100
Bismuth	200	20	0·2	1,000	100
Beryllium	1,000	300	5	180	50
Cobalt	1,500	300	40	35	8
Nickel	8,000	700	100	80	7
Zinc	10,000	200	40	250	5
Cadmium	50	5	0·5	100	10
Lead	1,000	100	16	60	9
Silver	5—10	2	0·1	50—100	20
Gold	0·2—0·5	—	0·005	40—100	—
Platinum	0·7	—	0·005	120	—
Lithium	500	—	65	8	—
Scandium	400	60	5	80	3—12
Gallium	400	100	15	27	7
Yttrium	800	100	131	26	3
Zirconium	5,000	—	90	26	—
Molybdenum	500	200	15	33	15
Indium	2	—	0·1	13	—
Tin	500	200	40	13	5
Thallium	5	1	0·3	17	3

Fig R17

Table 9.5. Rare Elements in Coal Ash

Element	Average Content in Coal Ash (g/ton)	Average Content in Earth's Crust (g/ton)	Factor of Enrichment
B	600	10	60
Ge	500	1.5	330
As	500	2	250
Bi	20	0.2	100
Be	45	2.8	16
Co	300	25	12
Ni	700	75	9
Cd	5	0.2	25
Pb	100	13	8
Ag	2	0.1	20
Sc	60	22	3
Ga	100	15	7
Mo	50	1.5	30
U	400	2.7	150

These consist of a central atom or ion (generally a metal) surrounded by a radicle which is an organic molecule which is an electron donor. (a ligand). An example is chlorophyl (See Fig. R18).

Some of the compounds which form chelates are /6/ primary amines, secondary and tertiary amines, oximes, imines, thioesters, keto groups, thioketo groups, hydroxyl groups and carboxyl groups. (the latter is very important in the case of humic substances which have acidic properties). Of course, not all of these substances are stable under natural conditions.

Porphyrin chelates are well known in petroleum and solid bitumen. /33, 34, 35, 36/ Petroleum contains particularly stable Ni and V porphyrins, /34/ which are often given all the credit for the presence of these elements. However, the amount of trace elements in petroleum is usually greater than the amount which the porphyrins present can accommodate. /33/ Therefore some other combination must also exist. Mason /30/ suggests that napthenic and sulphur containing compounds are responsible for holding Ni, V and perhaps other metals.

Porphyrins are easily detected, but only with sophisticated equipment. /35/. Fig. R19 from Dunning and Moore /35/ shows the structure of two typical porphyrins and their orientation at oil-water interfaces. These authors have written an excellent article on porphyrin research /35/ for the interested reader. They note that V porphyrins are found in the respiratory systems of some marine organisms, but that the bulk of V and Ni in petroleum porphyrins has displaced Mg and Fe from the original biogenic compounds such as chlorophyll. Fig R18, from Manskaya and Drozdova /6/ shows the possible path of transformation of chlorophyll into petroleum porphyrins.

Porphyrins are not common in coals and kerogen shales. Here humic acids (carboxylic groups attached to the humic skeleton) are the important complexing agents. Various metal humates exist in a regular form with a mineral name. Doplerite is a Ca-Mg-Fe humate /3/. Thucolite is a rare earth humate. /3/.

Fig R18

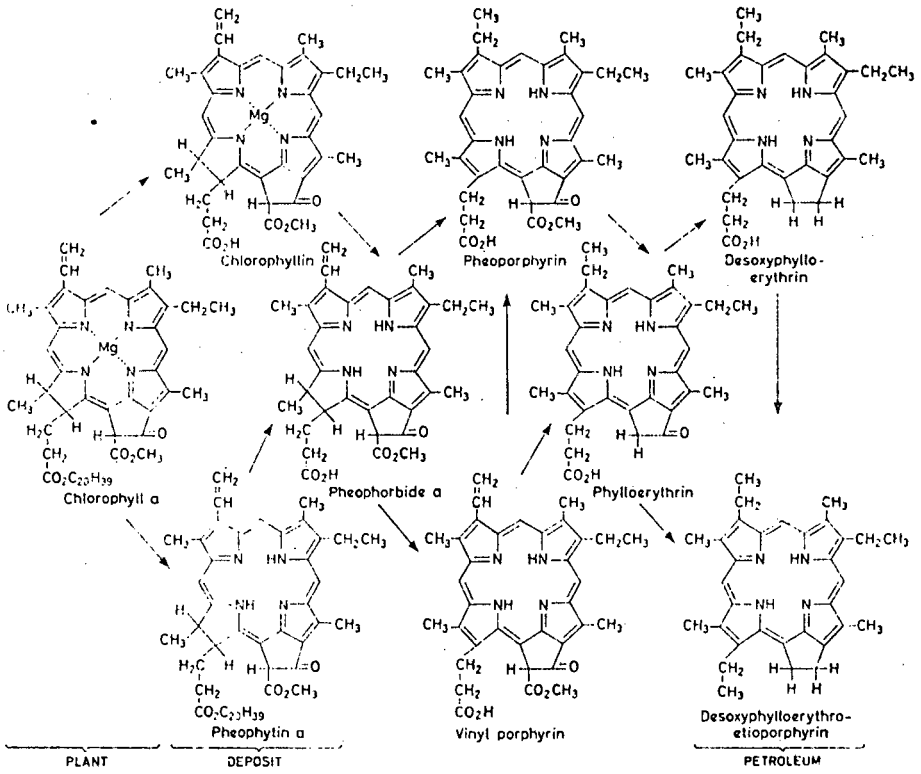


FIG. 50. Possible intermediates in the transformation of chlorophyll into petroleum porphyrins.

Fig R19

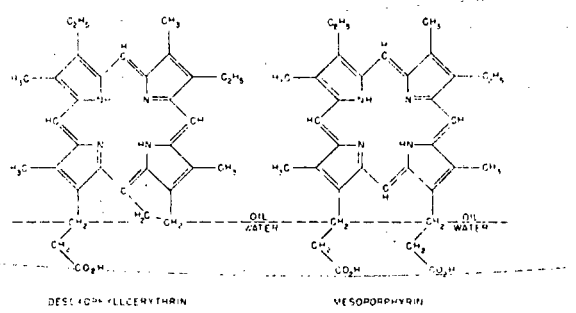


FIG. 3.—Structures of typical porphyrins and orientation at oil-water interface.

There have been many experimental studies on the nature of the absorption of elements by humic material. /3/. (See Fig. R3) It is known that anions are not appreciably absorbed. /3/. Several sorbtion sequences have been established and found to be only slightly dependent on concentration of the metal and pH. Some of these are:- /3/.

Fe^{2+} Cu^{2+} Fe^{3+} ; Li Na K Rb Cs (compare this with my findings for the alkali metals) Sr Ba.

The humic-metal bond is often very strong. For example, Mn, Fe and Cu are so firmly held by the humus of peat that plants growing on these deposits are severely deficient in these metals /39/.

What can we learn from the trace element content of organic matter? Undoubtedly these studies will, in time, shed light on the genesis and history of both the organic matter and the host rocks, but geochemistry has not made much progress in this direction as yet. According to Nicholls /29/, it is possible that the trace metal content of the organic fraction can be used as a paleosalinity indicator. He has found, empirically, that high concentrations of Cu, Pb and Sn in the organic matter of shales usually indicates a fresh-water origin, while high Ni and V in the organic matter indicates marine origin. He is careful to point out that experiments have shown that marine and terrestrial organic matter have very similar sorbtion characteristics for trace metals and so this observed difference in metal content is only a reflection of the availability of these elements in fresh and sea water respectively.

Fig. R20, from Keith and Degens /34/ compares the concentrations of several elements in organic matter from some marine and fresh water shales. Degens et al /17/ give the following list of elements enriched in fresh water and marine shales. Asterisks indicate very high concentration.

Fig R20

TABLE 2. Trace Elements Concentrated in the Organic Fraction of Marine and Fresh-Water Shales

(Data of Degens et al., 1957)

Element	Fresh-Water Shales, ppm			Marine Shales, ppm				Lower Limit of Detection
Sample No.	*110*	*114*	*135*	*291*	*297*	*299*	*302*	
Pb	400	150	100	40	50	40	150	(10)
Ni	20	25	20	150	100	70	80	(5)
Sn	30	40	20	7	5	5	10	(2)
Cu	500	1500	1000	150	100	150	800	(1)
Zn	400	600	1500	400	300	500	1000	(200)
Ag	2	5	2	2	8	...	2	(1)
Co	40	10	20	20	20	...	40	(10)
Mo	4	1	3	6	2	...	5	(2)
V	100	100	80	150	150	100	200	(10)

Other trace elements found (B, Ba, Be, Cr, Ga, Mn, Rb, and Sr) are not concentrated in the organic fraction relative to the raw shale.

Fresh Water	Marine
Pb	-
-	Ni
Sn*	Sn
Cu*	Cu
Zn*	Zn
Ag	Ag
Co	Co
Mo	Mo
V	V*

The reasons given for the variation between the two are:- /17/

1) Variation in availability of the metals in the sea and fresh water.

2) Variations in the absorption characteristics of different types of organism. For example, the Pb, Cu and Zn contents of peat moss are greater than the corresponding contents of marine plankton. /17/. (This view is not shared by Nicholls /29/)

3) Variation of post depositional absorption effects. i.e. the influence of ground water.

Degens et al warn that these paleosalinity indicators may be considerably upset by reworking of sediment or leaching of metals during diogenesis. /17/

Manskaya and Drozdova /6/ find that near shore oozes have higher Cu and Mn than those of the open sea, and that terrigenous ooze has more P, As, I, V, Cu and Mn than marine ooze.

- - - oOo - - -

To conclude this discussion on the role of organic matter in the geochemistry of the elements, I include some notes on the biogeochemistry of the elements which I determined in the organic separates.

Li.

There is a dearth of literature on organic lithium, but it is certainly rare in caustobioliths. Lithium has no known biological function /38/, but occurs in minute amounts in plant and animal tissue. Some plant ash is enriched in Li. e.g. tobacco up to 0.44% /38/.

Na.

Sodium is common in plants, but has no known essential function. /38/. Sodium is important in animals, but animals are unimportant in caustobioliths. Most of this animal Na is released as NaCl and returned to the ocean./38/. Na occurs in many caustobioliths, but is never enriched.

K.

Potassium is an essential element in both plants and animals /38/. The preferential absorption of K against Na in plants is very marked. Most of the K in plant ash can be extracted as the carbonate. /38/. Most of the K is released on decay /38/. K behaves similarly to Na in caustobioliths.

Rb and Cs.

Both are reported /38/ in traces in biological material, probably accompanying K. Rb seems to be concentrated in some plants, but is toxic to animals; Cs is apparently toxic to all life forms./38/ The content of Rb and Cs in caustobioliths is seldom reported and to my knowledge has never been reported to be concentrated. Neither is mentioned by Manskaya and Drozdova /6/ in the list they give of the elements concentrated by organic matter.

Mg.

Magnesium is essential to all life on earth because of its occurence in chlorophyl./38/ Mg is important in acaustobioliths. Dunning and Moore /35/ claim that heavy metals tend to replace Mg as the chlorophyll of the decaying plant is degraded to simpler porphyrins. Mg is often reported in caustobioliths, but is never generally concentrated.

Ca.

Calcium is a very important biological element /38/ but its occurrence is mainly acaustobiolithic. It is reported in small amounts in caustobioliths generally, and ofted in substantial amounts in younger materials like peat. It is fixed by humus, especially as Calcium Pectate, which is stable. /4/ It occurs in the humate "mineral" Doplerite, which may contain over 30% CaO. This explains why Ca is often present in coal in fair concentration. /4/

Sr.

Strontium follows Ca closely in general biochemistry, but on a smaller scale. Little is known about it in caustobioliths, but it is not reported to be concentrated. The Sr content of shales is greater than that of sandstones /24/, but this seems to be due to acaustobioliths.

Cr.

Chromium is not abundant in any organisms /4, 26/ and is toxic to plants. /38/ According to the literature, Cr is not heavily enriched in the reducing environment or in most of the carbonaceous rocks of the world. /26/ It is, however, strongly concentrated in the Kupferschiefer /26/ and its presence in caustobioliths seems to be related to post-humous absorption by humic substances. /26, 33/ According to Katchenkov, the level of Cr in the average shale (0.01%) is slightly greater than that in the average sandstone. He accounts for this as follows:

1) Shales have a higher proportion of mafic minerals.
2) Chemical absorption by the organic matter occurs in the sediment.

Mo.

Molybdenum is a dispersed element /6/ and although often reported in caustobioliths, the chemistry of this association is poorly known. /6/ Its concentration in sediments is related to the organic content, and it is also concentrated in bauxites. /6/ On average, a series of Russian coals /6/ had 20-30 p.p.m. Mo, with some specimins up to 1% MoO_3. Some Russian lignites have up to 0.5% Mo.

Limestones and samdstones very seldom concentrate Mo. Mo is most often enriched in the bituminous caustobioliths like petroleum /6/ and, on average, coals have a considerably lower concentration of the metal. /6/ Mo is an essential element in plants and animals /6/, especially legumes. It functions in coenzymes /38/. Studies of density fractionated carbonaceous shales of the U.S.S.R. /6/ showed that 16% of the total Mo was organically held. Most authors /6/ agree that the Mo is concentrated in the sediment at the time of formation, but the mechanism is obscure. It occurs frequently as the sulphide, /38/ indicating that, like Cr, its presence is due mainly to chemical absorption by humic substances.

Mn.

Manganese is a geochemically widespread element /33/ and its presence in caustobiolithic deposits is variable. It is an essential minor element in plants. Organic compounds are important mobilizers of the Mn ion, but most of the Mn transported this way ends up as MnO_2. /6/ Under acid conditions, Mn is usually leached out of sediments even if the Eh is low. /38/ Under alkaline conditions, it may concentrate in organic matter, but on the other hand, it may concentrate in the complete absence of organic matter. /38/

In most of the world's biruminous shales, it is depleted /26/, but in the Kupferschiefer it is relatively enriched, and appears to be related to the carbonate fraction. The average Mn content of shales (0.044 to 0.067%) is slightly more than that of sandstones. /24/

Fe.

Iron is necessary for plants and animals. /38/ It is needed in the synthesis of chlorophyll. It occurs in the porphyrin haemin, in animal blood. The element is essential to the Iron Bacteria, an important group of micro-organisms which sheathe themselves with iron hydroxide. They run on the energy of the reaction /38/:

$4FeCO_3 + O_2 + 6H_2O = 4Fe(OH)_3 + 4CO_2$ (H = -81 k cal)
and are therefore only important under oxidizing conditions. It has been demonstrated that humic acids can fix Fe, /3/ but in general Fe is depleted in caustobioliths /26/.

Co.

Cobalt is an essential trace element e.g. in Vitamin B12 /38/, which is a cordination complex of the metal. A naturally occuring organic compound of cobalt is reported from the Congo; $Na_2Co(CNS)_4 \cdot 8H_2O$. /38/ The relationship of Co to the organic content of caustobioliths is poorly known, but apparently variable. /26/ It is seldom greatly enriched. Manskaya and Drozdova /6/ give the following figures for Co in g/ton:

Earth's crust	Shales	Sandstones	Limestones.
23	10-50	1-10	0.2-2

Ni.

Very little Nickel reaches the sea from rivers, /38/ but meteorite dust probably contributes a fair amount of Ni to the ocean. /6/ Ni is widely reported in high concentration in caustobioliths /26, 33/. According to Zul'fugarly /33/ the Ni content of the caustobiolith is related to the type of organism forming the deposit. Ni is more concentrated in shales than in sandstones. /24/ It occurs widely in organisms, but according to Day /38/ there is little evidence that Ni has any biological function. The Ni porphyrins of petroleum are mentioned elsewhere in this work.

Cu.

Copper is probably an essential trace element for plants, but is seldom strongly concentrated in living organisms. There are exceptions. For example, the concentration of Cu in some species of plankton and in Spirogyra was mentioned earlier in this work. Certain other marine animals, plants and algae concentrate Cu. Generally the Cu content of land plants is low, but trees often concentrate Cu if it is present in large amounts in the soil. /6/

There are some species (mostly fungi and algae) which are poisoned by Cu. /38/

Soluble Cu salts are rapidly immobilized by humic matter, mainly as complex co-ordination compounds. For example, very high concentrations of Cu occur in some peat bogs in Rhodesia, which are fed by streams with above average Cu content. /6/ As one might expect, Cu is known as an element which readily forms a wide range of co-ordinated organometallic complexes. /6/ Copper is strongly concentrated in marine muds and in caustobioliths generally, usually in co-ordinated compounds. /26/ Some of the organically held copper may be converted to the sulphide by bacteria. /38/

The reported concentrations of Cu in caustobioliths has a wide range, usually from a few p.p.m to 10,000 p.p.m or more; for example the Kupferschiefer often has more than 1% Cu. /26/

Petroleum ash usually contains more Cu than coal ash, but generally the enrichment of Cu in petroleum is less marked than the enrichment of V or Ni. /24/

It appears that in most cases the concentration of Cu in kerogen and petroleum is related to the amount which was available at the time of formation, because humic materials very rapidly immobilize Cu ions. This was demonstrated in an experiment in the Bay of Naples /6/ where it was shown that humic matter rapidly removes practically all Cu from sea water.

Ag.

Silver apparently serves no biochemical function, but is concentrated by some plants and many marine animals. /38/ It is often found to be enriched in caustobioliths, /6/ especially black muds.

Au.

Gold is not normally sought in caustobioliths and little is known of its biochemical function.

It is concentrated by organic matter, however, and apparently /6/ Goldschmidt found appreciable quantities of Au related to carbon in marine basins, the Mansfeld bituminous shales and elsewhere. Humic acids form stable complexes with Au /6/ which are similar to the well known gold-thiocyanate complex.

Zn.

Zinc is an essential trace element in plants and many animals /38/ (e.g. in insulin). It is frequently reported in high concentrations in caustobioliths /6/. In the Permiam Phosphoria of the U.S.A. /26/ it reaches 1%, but in most carbonaceous sediments it seldom exceeds 250-300 p.p.m. /26/ In Wedepohl's study /26/, 30% of the samples of every organic rich Kupferschiefer had a Zn content lower than that of the average shale (100 p.p.m). An interesting feature of Zn distribution is its occurrence in similar amounts in petroleum and coal (unlike V, Ni and Cu).

Al.

Aluminium is apparently not usually an essential element for plants, but it does accumulate in certain species, although its function in them is unknown./38/ The ash of species of plant such as Symplocus, Orites and Lycopodium often has up to 33% Al_2O_3./26/ Al^{3+} ions are not very mobile /26/ and Al is readily fixed by humic acids. /3/ Al is present in most caustobioliths, but is never concentrated. The mineral mellite in brown coal is a hydrated aluminium salt of mellitic acid, a benzene hexacarboxylic acid.

Pb.

Lead in most carbonaceous sediments seldom exceeds 50 p.p.m /26/, but it is widely present in caustobioliths /26/ and can be concentrated to high levels. Although Pb is highly concentrated by some species (e.g. Spirogyra and some plankton) it is toxic to most animals and plants and its presence in organic deposits seems to be due to chemical rather than biochemical accumulation.

3.8 CONCLUSIONS.

1) A reliable method for separating and analysing the organic fraction of shales has been developed, but can be refined and expanded.

2) This study confirms the concentration, by organic matter, of certain metals in these predominantly Ecca sediments.

3) The Atomic Absorption Spectroscopy method of analysis is good, but bigger samples should have been used to reduce the dilution effect, in order to obtain more reliable results.

4) The loss of weight on ignition is not an indicator of the metal content of the shale.

5) The metals that are being concentrated are present in some sub-fraction of the organic fraction, which is not necessarily related to the total organic content.

6) Inter-element correlations within the organic fraction are not very instructive.

7) The well known geochemical correlations, like K-Rb, do not hold in the organic fraction.

8) The theoretically computed values, like "Co" and "PER" and the graphical methods used in this work, are a useful aid in the study of the element distribution in the organic fraction.

9) The results of the analysis for several samples are unusual. These would be of considerable interest if they could be shown to be accurate. Further work is needed.

10) Generally, the elements studied in this work behaved predictably, with the exception of Rb, Cs and Ca, which are all higher in my samples than might be expected from the literature on similar materials. These high concentrations may have been the result of some unusual set of circumstances existing during or after the deposition of these sediments.

11) The organic fraction apparently concentrates gold. This should be checked.

12) The high Cu and Pb values indicate a fresh water origin for these shales, but the high Ni values indicate a marine origin. Further work is needed to establish whether the trace element content of the organic fraction of Ecca shales can be used as a paleosalinity test.

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